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CONTENTS.

PAGE

One Hundred and Thirty-First General Meeting :—
Gas In Relation to Oil Production, by B. J. Ellis .. 2
Discussion : Dr. A. E. Dunstan, Prof. E. R. Lilley, Prof. V. C. Illing, Capt. D. Comins, Dr. A. Wade and Mr. L. Owen 30
Reply by Mr. B. J. Ellis.. 37
Contributed Discussion : Mr. L. Owen 40
Reply by Mr. B. J. Ellis.. 41

Persian Branch :—
The Vapour Pressure Curves of Motor Spirits, by P. Meyer, B.Sc., A.I.C... 42

Knock-Rating of Motor Fuels. Note on Experiments carried out in 1930. By the Sub-Committee of the Institution of Petroleum Technologists on Knock-Rating of Motor Fuels 69

Reviews : "Report of the Fuel Research Board for the Year ended March 31, 1930"; "British Chemicals and their Manufacture," by Association of British Chemical Manufacturers; "Official Directory of the British Chemical Plant Manufacturers' Association .. 72

Methods of Increasing the Yield from Oil-Sands, with Special Reference to Repressuring, by L. C. Stevens, B.Sc. .. 73

Luminous Stationary Flames : the Quantitative Relationship between Flame Dimensions at the Sooting Point and Chemical Composition, with Special Reference to Petroleum Hydrocarbons, by S. T. Minchin, B.Sc., A.I.C. 102

Hydrogenation of Petroleum Oils, by Ralph H. McKee and Antoni Szayna 121

A Modified Absorption-Distillation Method for the Analysis of Cracked Gasolines, by Charles C. Towne 134

Current Petroleum Notes : Imports of Methyl Alcohol; Sea Transport by Molten Bitumen; Use of Waste Natural Gas; Tanker Chartering 142

Rumanian Branch :—
Fourth Annual Dinner 143

The Chemical Aspect of Drilling Muds, by Alexander Duckham, F.C.S. 153

Sixth International Road Congress, October 6-11, 1930, by P. E. Spielmann, Ph.D., F.I.C., B.Sc., A.R.C.S., F.Inst.P. 183

CONTENTS.

PAGE

The Reaction of Olefines with Sulphuric Acid, by W. R. ORMANDY, D.Sc., F.I.C., F.C.S., M.I.A.E., and E. C. CRAVEN, B.Sc., F.C.S. 185

Current Petroleum Notes: Petroleum Developments in Africa, Argentine, Bolivia and Chile, California, and Russia 188

Reviews: "On the Determination of the Empirical Formula of a Hydrocarbon," by E. W. WASHBURN; "Compressibility and Thermal Expansion of Petroleum Oils in the Range 0° to 300° C." by R. S. JESSUP 190

Annual Report of Council, 1930-31 191

Eighteenth Annual General Meeting 200

Hydrated Lime and Diatomaceous Earth ("Diatomite") in Oil Well Cement, by ALEXANDER REID, M.A., B.Sc. .. 211

The Catalytic Addition of Gaseous Hydrochloric Acid to Unsaturated Hydrocarbons, by W. J. PIOTROWSKI and J. WINKLER 225

A Constant Level Consumption Meter for Lamps, by R. DOWNER 242

Current Petroleum Notes: Petroleum Operations in New Zealand; Production of Natural Gas Gasoline; Production of Liquefied Petroleum Gases 246

Reviews: "Erdol und Verwandte Stoffe," by R. KOETSCHAU; "Elements of Chemical Engineering," by W. L. BADGER and W. L. MCCABE; "Applied Geophysics," by H. SHAW; "Reports of the Progress of Applied Chemistry, 1930," by Society of Chemical Industry; "Chemical Engineering and Chemical Catalogue," by D. M. NEWITT 247

One Hundred and Thirty-Second and One Hundred and Thirty-Third General Meetings:—

Symposium on Salt Domes:—

Salt Domes of North Germany, by JAMES ROMANES, F.G.S. 252

Salt—Some Depositional and Deformational Problems, by G. M. LEES, M.C., D.F.C., Ph.D., F.R.G.S., F.G.S. 259

Salt Domes of Texas and Louisiana Gulf Coast, by FREDERICK G. CLAPP, S.B., F.G.S., F.G.S.A., F.A.G.S., M.A.A.P.G. 281

Salt Domes in Persia, by J. V. HARRISON, B.Sc., F.G.S. 300

PAGE

One Hundred and Thirty-Second and One Hundred and Thirty-Third General Meetings—*continued.*

Symposium on Salt Domes—*continued.*

Intrusive Salt Bodies in Coastal Asir, South-Western Arabia, by ARTHUR WADE, D.Sc., A.R.C.Sc., F.G.S., M.Inst.M.M., F.Am.G.S. 321

Origin of the Salt Domes of the Gulf Coastal Plain of the United States, by E. DE GOLYER.. 331

Moot Points in Salt Dome Theory, by LAUNCELOT OWEN, A.R.C.S., A.R.S.M., D.I.C., M.Inst.M.M., F.G.S. 334

A Contribution to "Salt Dome" Geochemistry, by MURRAY STUART, D.Sc., Ph.D. 338

Salt Occurrences in Egypt, by HAROLD DABELL .. 346

Discussion: Dr. E. R. LILLEY, J. ROMANES, Mr. E. H. CUNNINGHAM CRAIG, Mr. T. DEWHURST, Prof. V. C. ILLING, Dr. A. WADE, Mr. B. K. N. WYLLIE, Mr. T. R. H. GARRETT, Dr. J. A. L. HENDERSON, Dr. E. PARSONS and Dr. W. A. MACFADYEN 348

Replies by Dr. MURRAY STUART and Mr. E. DE GOLYER 369

The Salt Dome Area West of Celle, Germany, by Dr. CARL SCHMIDT 372

Salt Dome Studies by Geo-Electrical Methods, by KARL SUNDBERG 376

Geophysical Investigations carried out in the Salt-dome Areas of the Gulf Coast of Texas and Louisiana, by Dr. CARL SCHMIDT 381

Current Petroleum Notes: Motor Fuel Characteristics; Carbon Black Production; Re-Forming Natural Gas; Canadian Petroleum Production 384

Correspondence *re* "Gas in Relation to Oil Production" from Mr. B. J. ELLIS 385

Review: "Entstehung, Veredlung und Verwertung der Kohle," by W. PETRASCHECK and others.. 386

One Hundred and Thirty-Fourth General Meeting:—

Fuel Testing in Slow and High Speed Diesel Engines, by L. J. LE MESURIER, M.I.N.A., M.Inst.Mar.Eng., and R. STANSFIELD, A.M.Inst.C.E. 387

Discussion: Dr. A. E. DUNSTAN, Mr. J. KEWLEY, Dr. F. B. THOLE and Mr. J. L. CHALONER 418

Reply by Mr. L. J. LE MESURIER and Mr. R. STANSFIELD 421

Contributed Discussion: Dr. F. H. GARNER 423

Reply by the authors 423

CONTENTS.

PAGE

One Hundred and Thirty-Fifth General Meeting :—

Recent Developments in Fractional Distillation, by C. H. S. EDMONDS, M.Am.Soc.Mech.E., M.Am.Pet.Inst. 425

Discussion : Mr. J. KEWLEY, Mr. G. H. COXON, Mr. A. A. ASHWORTH, Dr. F. H. GARNER, Mr. E. LAWSON LOMAX, Dr. F. B. THOLE and Mr. C. R. SCOTT HARDY 443

Reply by Mr. C. H. S. EDMONDS 449

The Corrosive Effect of Gasolines and Motor Benzoles on Copper, by F. H. GARNER, Ph.D., M.Sc., F.I.C., and E. B. EVANS, M.Sc., A.I.C. 451

Current Petroleum Notes : Turner Valley, Alberta ; The Oil Well at Hardstoft 464

Reviews : "The Action of Hydrogen on Coal," by I. A. CRAWFORD, F. A. WILLIAMS, J. G. KING and F. S. SINNATT ; "Report of Test by Director of Fuel Research on a Retort of the Bussey Coal Distillation Co.".. .. 465

One Hundred and Thirty-Sixth General Meeting :—

The Present Position of Knock Testing Standardization :—

Standard Fuels, by C. H. BARTON, M.A., A.I.C. .. 468

Engine Types and the C.F.R. Standard Engine, by C. H. SPRAKE 471

Methods of Test and Precautions to be Observed, by R. STANSFIELD, A.M.Inst.C.E. 476

Discussion : Mr. J. KEWLEY, Dr. F. B. THOLE, Mr. W. G. ADAM, Mr. W. A. WHATMOUGH, Mr. A. T. WILFORD, Dr. F. H. GARNER and Mr. T. R. H. GARRETT and replies by the authors 481

Trinidad Branch :—

The Funnel Meter as an Aid to Production, by NIELS MATHESON, M.Am.I.M. & M.E. 485

Discussion : Mr. G. H. SCOTT, Mr. C. E. CAPITO, Mr. W. J. C. COOKE, Mr. J. RUTHVEN-MURRAY and Mr. A. FRANK DABELL 493

Reply by Mr. N. MATHESON 495

Rumanian Branch :—

Small Well Production Problems, by A. H. CHAPMAN .. 498

Empirical Formulæ for the Production Curves of Oil from Wells, by LAUNCELOT OWEN, A.R.S.M., A.R.C.S., D.I.C., M.Inst.M.M., F.G.S. 500

PAGE

Decomposition of Ethylene by Heating under High Pressure, by H. I. Waterman and A. J. Tulleners 506

425 Injection, Ignition and Combustion in High-Speed Heavy-Oil Engines, by S. J. Davies, Ph.D., M.Sc., and E. Giffen, M.Sc. 511

443 Current Petroleum Notes: Benzine from Turner Valley Gas;
449 New Refineries in Canada; Cracking Plants in the U.S.A.; Properties of California Crudes 515

451 Reviews: "A Monograph of Viscometry," by G. Barr;
"The Examination of Fragmental Rocks," by F. G. Tickell; "The Oil Exploration Work in Papua and
464 New Guinea conducted by the Anglo-Persian Oil Company on behalf of the Government of the Commonwealth of Australia, 1920-1929" 516

The Ermelo Torbanite as a Source of Oils in the Union of
465 South Africa, by William Bleloch, M.Sc., Ph.D. .. 521

The Determination of Mean Molecular Weights of Lubricating Oils by Improved Cryoscopic Methods, by N. G. Gullick, A.R.C.S., B.Sc., D.I.C. 541

468 The Total Heat and Specific Heat of a Series of Fractions of Petroleum Oil, and their Relation to other Properties,
471 by H. R. Lang, Ph.D., F.Inst.P., and R. Jessell, B.Sc., A.Inst.P. 572

476 Current Petroleum Notes: Preventing Losses of Gasoline by Evaporation; Motor Gasoline Survey; Acid Bottle Inclinometers 584

Note on the Specific Heat of some Crude Oils and their
481 Residues when Topped to 100° C., by H. R. Lang, Ph.D., F.Inst.P. 585

Trinidad Branch:—

485 The Chemical Aspects of Drilling Muds, by Alexander Duckham, F.C.S.

93 *Discussion:* Mr. J. L. Harris, Mr. A. G. V. Berry,
95 Mr. Moore, Mr. A. H. Richard, Mr. J. W. Knights, Mr. H. D. Fletcher, Col. H. C. B. Hickling, Mr. B. M. Craig, Mr. R. Godfrey, Mr. H. C. W. Johnston,
98 Mr. A. P. Chamberlain, Mr. H. S. Conder, Mr. G. H. Scott, Mr. R. N. Kirby, Mr. W. J. C. Cooke, Mr. C. C. Wilson and Mr. A. Frank Dabell 592

Reply by Mr. Alexander Duckham 605

00 *Contributed Discussion:* Mr. H. F. Warrington Morris 608

PAGE

Rumanian Branch :—
Open discussion on "Behaviour of Restricted Wells," by Mr. G. Elias, Mr. Boaden, Mr. H. F. Crooks, Mr. C. Leitch and Mr. Masterton 611
The Removal of Weak Organic Acids from Oils by Treatment with Caustic Alkali, by P. Meyer, B.Sc., A.I.C... .. 621
Current Petroleum Notes: East Texas Crudes; Trinidad.. 629
Review: "Petroleum Development and Technology, 1931," by American Institute of Mining and Metallurgical Engineers 630
Thirteenth Annual Dinner 633
One Hundred and Thirty-Seventh General Meeting :—
Apparatus for the Sweating of Paraffin Wax, by H. L. Allan 657
Discussion: Mr. J. Kewley, Mr. E. Thornton, Mr. J. E. Hackford, Mr. A. A. Ashworth and Mr. R. Pitkethly 668
Reply by Mr. H. L. Allan 673
Reply by Mr. W. J. Wilson 677
Trinidad Branch :—
Precautions Taken in Drilling Wells in Persia with Cable Tools, by C. Erik Capito, O.B.E., M.Inst.C.E. .. 678
Discussion 684
Reply by Mr. C. E. Capito 684
Control Methods in Fractionators, by S. S. Smith 686
Current Petroleum Notes: Alberta Tar Sands; Canadian Oil Production; Turner Valley Natural Gas 694
Reviews: "Hydrogenation of Organic Substances, including Fats and Fuels," by C. Ellis; "A History of the British Chemical Industry," by S. Miall; "Report of Committee D-2 on Petroleum Products and Lubricants," by A.S.T.M.; "Report on Tour of Inspection of the Oil Fields of the United States of America and Argentina, and on Oil Prospects in Australia," by W. G. Woolnough 694
One Hundred and Thirty-Eighth General Meeting :—
The Dilution Theory of Detonation, by I. A. J. Duff, B.A., A.M.Inst.C.E. 697
Discussion: Mr. J. Kewley, Dr. E. Mardles and Mr. R. Stansfield 721
Reply by Mr. I. A. J. Duff 726
Contributed Discussion: Mr. E. C. Craven, Dr. G. B. Maxwell, Mr. E. S. L. Beale and Dr. V. Henny .. 728
Reply by Mr. I. A. J. Duff 734

CONTENTS.

PAGE

On an Asphalt Ring from Ur of the Chaldees, by J. E. Hackford, B.Sc., F.I.C., F.C.S., S. Lawson and P. E. Spielmann, Ph.D., F.I.C., B.Sc. 738

Trinidad Branch :—

Economy Symposium :—

Research, by Arthur G. V. Berry 741

Means of Effecting Economy, by H. A. Bennett .. 742

Sunday Labour, by J. L. Harris 742

Conservation and Re-treatment of Heavy Mud, by E. Cooper Scott, M.C., B.Sc. 743

Economy in Drilling Time, by G. A. Richards, M.A. 745

A Factor of Economy, by J. T. Potter.. 746

Salvage, by H. D. Fletcher 747

Casing, by L. A. Bushe 748

Coring is Cheaper than Drilling, by C. C. Wilson, A.R.S.M. 749

Core Samples, by P. W. Jarvis 751

Salvage and Reconditioning of Material, by A. J. Ruthven-Murray, M.A., B.Sc., F.G.S. 752

False Economy, by A. F. Dabell, M.I.Mech.E. .. 754

Discussion : Mr. Van Achterbergh, Mr. L. A. Bushe, Mr. C. E. Capito, Mr. Fletcher, Mr. A. H. Richard, Mr. A. Chadwick, Mr. G. H. Scott, Mr. J. L. Harris, Mr. A. J. Ruthven-Murray and Mr. A. Frank Dabell 755

Standardization in Drilling and Well Pumping Equipment, by R. N. Kirby 759

Detonation in Internal Combustion Engines, by A. P. Chamberlain, B.Sc. 759

Current Petroleum Notes : Industrial Alcohol in South Africa ; New Alberta Oilfield 760

Review : "Petroles Naturels et Carburants de Synthese," by A. Graetz 760

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CONTENTS.

	PAGE
Council and Officers	i-ii
General Notices :—	
Copyright	iv
Issue of Journal	iv
Change of Address	iv
Papers and Articles	iv
Binding of Journals	iv
Reprints of Papers	iv
Abstracts	iv
Medals	v
Research Fellowship	v
Benevolent Fund	v
Appointments Register	v
Library	v
Advertisements	vi
Personal Notes and Special Notices	vi-viii

PAGE

Gas in Relation to Oil Production. By B. J. Ellis .. 2

Persian Branch :

The Vapour Pressure Curves of Motor Spirits. By P. Meyer, B.Sc., A.I.C. 42

Knock-Rating of Motor Fuels. Note on Experiments carried out in 1930 69

Books Received 72

Abstracts .. .. 1 A

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS

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Issue of Journal. The Journal is issued in twelve parts per volume, commencing in January of each year. The Title Page, Table of Contents and Index to each volume are published in the second issue of the succeeding volume.

Members whose subscription is not in arrear receive the Journal free of cost, and additional copies are charged at the rate of 7s. 6d. per part, unless otherwise stated. A member whose subscription is not paid by March 31st of the year for which it is due is considered to be in arrear.

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Galley proofs of the paper to be read at a General Meeting are available at the time of the meeting, but members desirous of receiving such galley proofs in advance should apply to the Secretary.

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paper only can be supplied with uncorrected galley proofs at a charge of 10s. per annum per copy, payable in advance.

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The Fund is raised by voluntary annual subscriptions, donations, and bequests, and all contributions should be sent to the Secretary of the Institution at Aldine House, Bedford Street, London, W.C. 2. The Fund is administered by the Council through the Benevolent Fund Committee, and all applications in connection therewith must be made on a special form which can be obtained from the Secretary of the Institution.

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PERSONAL NOTES OF MEMBERS AND SPECIAL NOTICES.

It is suggested that members send information regarding their movements to the Secretary, for insertion under this heading.

Mr. GEORGE BARCLAY is home from Burma.
Mr. R. L. C. BLEECK has returned from Persia.
Mr. A. P. CHAMBERLAIN has left for Trinidad.
Mr. D. T. JONES is in Persia.
Mr. P. KERR is in Japan.
Ing. J. MARTYNIK has returned to Germany.
Mr. H. MILLIGAN has left Rumania and is in California, U.S.A.
Mr. J. M. PENNY has left Demerara and is now in Trinidad.
Mr. JOHN C. RICHARDS is returning from Africa.
Dr. G. SHEPPARD has returned to Ecuador.

The Secretary would be glad to hear of the whereabouts of the following members :—C. A. BAUDUIN, A. E. O. COOKE, W. G. B. COUTTS, B. DVORKOVITZ, W. M. GRAY, W. J. HARRIS, L. B. HOLLOWAY, C. E. JOBLING, A. F. C. PARKER, NAND LAL PASI, W. W. SCOTT, W. E. SHEPHERD, R. K. VAN SICKLE and F. E. G. WATSON.

DINNER CLUB.

The attention of members is drawn to the Dinner Club of the Institution. This Club holds informal dinners after each General Meeting of the Institution and members may invite guests. Those desiring to receive notice of these dinners, are requested to inform the Secretary of the Institution.

NOMINATIONS FOR MEMBERSHIP OF THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

The following have been nominated for membership of the Institution of Petroleum Technologists and their Application Forms may be seen at the Offices of the Institution :—

As Members :—	PROPOSED BY	SECONDED BY
HOTHAM, Enoch, Chemist, "Westgarth," Hull Road, Cottingham, E. Yorks.	Harold Moore.	R. B. Hobson.
LINDOP, Elliot David, Chemical Engineer, 1, Shenley Road, Hounslow, Middlesex	Harold Moore.	R. B. Hobson.
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RENDEL, Terence Blair, Engineer, c/o. Shell Petroleum Corpn., Wood River Refinery, Wood River, Ill., U.S.A.	F. L. Garton.	F. W. L. Tydeman.
As Student :—		
BAKER, William James, Engineer, "Braunton," Cadbury Road, Sunbury-on-Thames	F. B. Thole.	W. H. Thomas.
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CLAYTON, Henry Oswald, Chemist, 21, Victoria Avenue, Didsbury, Manchester	A. E. Dunstan.	F. B. Thole.
JONES, Norman Ellathorne, Chemist, 59, Queen's Road, Richmond, Surrey	J. S. Jackson.	David L. Samuel.
LEE, Hubert William Henry, Chemist, 108, Faraday Road, Wimbledon, London, S.W. 19 ..	J. S. Jackson.	David L. Samuel.

JOURNAL OF THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

Commencing with this number the Journal will be published in twelve monthly parts per annual volume. The price per part will remain at 7s. 6d. and the annual subscription will be £3 13s. 6d.

THIRD INTERNATIONAL CONFERENCE ON BITIMUNIOUS COAL.

The Carnegie Institute of Technology announces that a Third International Conference on Bituminous Coal will be held at Pittsburgh, November 16th to 21st, 1931.

The programme will include papers on the carbonisation, liquefaction, and gasification of coal; by-products; the mechanism of combustion; cleaning of coal and its preparation for the market; pulverised fuel, power plants; domestic heating; etc., and scientists from all countries are invited to take part.

Dr. Thomas S. Baker, President of the Carnegie Institute of Technology, is at present visiting Europe to confer with fuel technologists who may be considering taking part in the Conference, and his address, until early February, will be care of the Guaranty Trust Company, 4 Place de la Concorde, Paris.

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THE INSTITUTION OF PETROLEUM TECHNOLOGISTS.

THE ONE HUNDRED AND THIRTY-FIRST GENERAL MEETING of the Institution of Petroleum Technologists was held on Tuesday, December 9th, 1930, at the Royal Society of Arts, John Street, Adelphi, London, W.C.2, Dr. A. E. DUNSTAN (President) occupying the chair.

The Secretary read the names of members elected and candidates nominated for election, as follows :—

The following were elected on November 28th, 1930 :—

As Members.—William Ernest Victor Abraham, George Calzavara, Robert Webb Farmborough, Andre Graetz, George Hulme Hubbard, Theodore Alaric Peck, Francis Martin Potter.

As Transference to Members.—Albert Harold Seagrim, Henry N. L. C. E. C. de Wilde.

As Associate Members.—Jean Georges Berteloot, George Philip Bowring, Max Capper, Eric Carter, Leslie Vincent Woodhouse Clark, (Miss) Winifred Sarah Elizabeth Clarke, Stanley Owen Connor, Normal Russell Fowler, Noel William Grey, Ernest Noel Hague, Donald George Hitt, Thomas Reginald Palmer, Robert George Perry, Walter Sigg, Arthur Noel Lucie-Smith, Colin McLuckie White.

As Transference to Associate Members.—Mauritz Julius Bernard de Blank, George Dickinson, Douglas Jonathan Paul, Jesse Ossowa Tanner.

As Students.—John Greaves Beastall, Richard Vernon Browne, John Leslie Howard, Geoffrey Howard Hunter-Brown, John Alexander Pryde, Tadeusz Rudolf Rogala.

As Associates.—Douglas Oliver Bremner, George Norton Critchley, Roland Doumin, Alexander P. Shearer, Thomas Gilbert Webb.

The following were nominated on November 11th, 1930 :—

As Members.—Percy George Hamnall Boswell, Ionel I. Gardescu, William Ladislas Gomory, Eric Stanley Hillman, Edward Alfred Hunting, Arthur John Wright.

As Associate Members.—Roland Edwards Hales, Harold Leslie Lyne, James Ness Rodger.

As Transference to Associate Member.—Herbert Richard Lovely.

As Student.—Laurence George Melville Roberts.

As Associates.—Thomas Moore Hickman, John Arthur Reed Pepper.

The following were nominated on December 9th, 1930.

As Members.—Robert Illtyd Lewis, Arthur Richard Pattisson, Jack Francis Mahon Taylor, Sijbren Tijmstra.

As Transference to Member.—Mostafa Allam.

As Associate Members.—William Lawrence Bouch, Richard Godfrey, Arthur Henry Goodliffe, Vacey Vivian Linnington Hope, Herbert Leonard Joseph Hunter, Eric Rofe Styles, Alfred Reginald Thomas.

As Transference to Associate Members.—Norman Macdonald Brodie, Kenneth Brebner Ross, Geoffrey Stewart Taitt.

As Students.—Michael Abramovitch, Geoffrey Melvin Barrett, Arthur Evans, Percival George Higgs, Giles Philip Eliot Howard, Hugh John Marks, Leslie Benjamin Sweetland, William Roy Wright.

As Associates.—Adolph Freiman, Michael Hamel-Smith, Malcolm Alexander Campbell MacNeill.

THE PRESIDENT announced that a letter had been received stating that the Privy Council had been unable to recommend to His Majesty the granting of a Royal Charter to the Institution.

The following paper was then read :

Gas in Relation to Oil Production.

BY B. J. ELLIS (Member).

The publication two years ago of S. C. Herold's work, entitled "Analytical Principles of the Production of Oil, Gas and Water from Wells," marked a decided forward step in the knowledge of the relationship between gas and oil in production, and gave considerable impetus to the efforts then being made by production engineers, physicists and others connected with oil fields to model their producing methods on an ideal of maximum ultimate rather than of maximum daily production.

The problem of production would be sufficiently difficult if it were merely one of mechanics, but as it is complicated also by economics with its ever-changing values of products and costs of production, it resolves itself into a compromise between the mechanical best and practical economic requirements.

Unfortunately, there is still some doubt as to the absolute truth of Herold's theories, and the characteristics of oil reservoirs and their contents vary so greatly that there is danger in dogmatising even as to what the mechanical ideal is. Practical criteria of some sort have, however, to be set up as goals towards which to work, and this paper is an attempt to formulate those which should govern the production of gas with oil.

Herold's thesis and his findings deal solely with the pure mechanics of production of simple perfect gases and liquids from hypothetical homogeneous reservoirs. Such conditions are of course not experienced in oil fields, and the first step therefore will be to examine something of the three variables, oil, gas and the reservoir, as they exist in nature. Thereafter Herold's theories will be briefly described and an attempt will be made to relate them to natural conditions. The theory of repressuring and gas drive will be

considered, as will its practical application, and a possible method of increasing the recovery of oil by a modified form of gas drive will be discussed.

Nature of Gas and Oil.

Natural gas found associated with oil is a mixture of a number of hydrocarbon compounds as follows :—

Gas.	Critical temperature.	Critical pressure gauge.
*Methane	—185° F. ..	825 lb.
Ethane	+ 85° F. ..	678 lb.
Propane	+225° F. ..	620 lb.
Butane	+320° F. ..	535 lb.
Pentane	+400° F. ..	465 lb.
Hexane	+470° F. ..	415 lb.

Owing to their low critical temperatures, methane and ethane will always exist as gases in natural reservoirs. On the other hand, propane and butane will exist as liquids at the pressures and temperatures usually found together in reservoirs, and will be converted to gases in the reservoir only if pressure is sufficiently released, or when brought to the surface and reduced to N.T.P. The remaining gases will always exist as liquids in the reservoir except as far as their container and associated gases allow them to vaporise.

To make one cubic foot of liquid the following quantities at N.T.P. for the first four gases are required :—

*Methane	620	cu. ft./cu. ft. liquid.
Ethane	355	„ „
Propane	277	„ „
Butane	238	„ „

The extent to which these gases are soluble in crude oil varies with the pressure, temperature and the nature of the crude, and no average figures can be given.

The gases in solution behave as liquids and, when dissolved in a crude oil, increase the volume and lower the specific gravity, viscosity and surface tensions just as if so much of their various liquids had been added. The specific gravity of the gases as liquids are as follows :—

*Methane	0·416 sp. gr.
Ethane	0·446 „
Propane	0·535 „
Butane	0·600 „

Compressed, liquefied and dissolved gases have potential energy relative to N.T.P. Oils which are liquids at N.T.P. have no such energy.

* These figures were obtained from Mr. Jacomini, of Messrs. C. F. Braun & Co.

To obtain some idea of the energy available, assume a field 8 sq. miles in extent with a sand 200 ft. thick having a pore space of 25 %, one-sixteenth of which is filled with free gas at 500 lb. per sq. in. and the remainder with oil of specific gravity 0·80 containing 7 % dissolved methane 1% dissolved ethane and 2 % liquefied propane, the temperature of the reservoir being 150° F. at a depth of 4000 ft. from the surface. The following figures can then be calculated :—

†Total pore space	.. ..	11,151,360,000	cu. ft.
„ free gas space	.. ..	696,960,000	„
„ oil space	.. ..	10,454,400,000	„
„ weight of oil	.. ..	233,357,000	tons.
Potential energy of free gas	.. ..	349	ft.-tons/ton of oil.
„ „ methane	.. ..	4954	„ „
„ „ ethane	.. .. ..	405	„ „
„ „ propane	.. ..	694	„ „
Total potential energy	.. ..	6403	„ „

The pressure necessary to liquefy propane at 150° F. is about 260 lb. per sq. in., so that unless or until the pressure on the oil in the reservoir drops to 260 lb. per sq. in., this fraction will not give up its energy.

The space occupied by the free gas is 6·25 % of the total space, while that occupied by the dissolved and liquefied gas is 9·38 %. In the example therefore 1 cu. ft. of dissolved gas has 11·5 times the energy of 1 cu. ft. of the free gas.

Nature of Reservoirs.

The reservoir is invariably of porous rock bounded on the top by an impervious rock layer and generally a similar stratum forms the bottom. Both top and bottom confines usually take the form of distorted inverted bowls, the oil and gas being held in the top of the porous rock between the two by water under pressure. Water therefore forms the remaining boundary of the container, and its head has created the pressure under which the oil and gas exist.

Nature of Reservoirs Under Production.

Reservoirs under production fall into two main divisions :—

1. Those in which the external forces, the water head acting below and the pressure of the free gas acting above, can cause movement of the oil in bulk at a rate proportional to the rate at which it is produced, and

2. Those in which the external forces cannot cause movement of the oil in bulk except at a rate so low as to have no effect on production.

† See Appendix I.

In the former division the whole of the potential energy associated with the free gas, the water and the gas dissolved and otherwise carried with the oil is exerted in production, whereas in the latter, only that energy associated with the gas dissolved and otherwise carried with the oil is available.

If, during production from a reservoir in the first division, the resistance to movement of the oil and gas in bulk increases, or the external forces decrease to such an extent that the rate of movement of the oil in bulk ceases to bear a relation to the rate of production, the reservoir changes over to the second division.

The first division of reservoirs is divided by Herold into two types :—

1. Those in which the external energy is replenished as used and therefore exerts a constant force, and

2. Those in which the external energy wastes with production and exerts an ever-decreasing force.

Herold designates the first type as " Reservoirs under Hydraulic Control," while the second he calls " Reservoirs under Volumetric Control."

The second division of reservoirs is all of one type named by Herold " Reservoirs under Capillary Control."

Hydraulic Control.

Consider a reservoir of the type shown in Fig. 1.

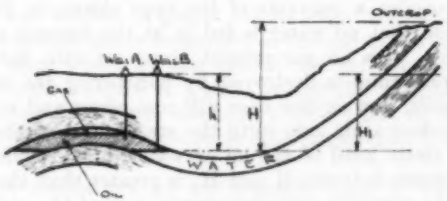


Fig. 1.

Under static conditions the water head will exert a definite pressure on the oil and gas in the dome. When the equilibrium is destroyed by puncturing the reservoir by a well or wells, flow will commence and will continue as long as the static head of the water, H, is greater than the static head of the oil, h, plus the friction of movement of the oil and water through the strata and the well to surface. Under " Hydraulic Control " the static head of the water remains constant, as water is continually fed in at the outcrop and, provided the friction head remains constant, the rate of production remains constant.

It is a *sine qua non* of "Hydraulic Control" that the ability of the water to enter the reservoir is as great as the ability of the oil and gas to leave it. If the gas with the oil takes any part in production, it must be a subordinate part within that limit. By assisting oil flow up the well it may reduce the static head of the oil and allow of an increased rate of production from a given number of wells, but the new static head plus the new friction head of the oil at the altered rate cannot be less than the constant static water head less its friction head at the new rate. Should it, by frothing or otherwise, increase the resistance to movement of oil through the strata, the rate of production for the given number of wells will be decreased, but a new condition will speedily be attained. It is clear, therefore, that whatever effect the gas with the oil has on production, it is a constant effect for a given condition of production. Once the steady flow condition has been attained, oil and gas will flow at a constant rate until all the oil, excluding oil adsorbed by the pore spaces, is produced, and thereafter water will flow instead at a similar but not necessarily at quite the same rate.

The gas in the top of the dome will expand and do work in producing the oil until the steady flow condition is reached, when it will take no further part.

Volumetric Control.

Again, consider a reservoir of the type shown in Fig. 1, with the exception that no water is fed in at the outcrop and, in the first instance, with no gas present above or with the oil.

When equilibrium is destroyed by puncturing the reservoir by a well or wells, flow in this case will commence and will continue at an ever-decreasing rate until the static head of the water H_1 equals the static head of the oil or water, h. Provided that the volume of water between H and H_1 is greater than the volume of the oil in the reservoir, complete production of the mobile oil will occur.

Now consider the same system, but with gas above and associated with the oil in the reservoir. Here the static head of the water will be balanced by the pressure in the reservoir, and, as production takes place, this balance will be maintained. The water head decreases as before and the reservoir pressure must likewise decrease, thus allowing the gas to expand and do work in moving the oil through the strata and up the well.

The gas and water have equal energy at all stages of production and the work of production will therefore be shared equally by each. Production of all the mobile oil in the reservoir will occur

if the sum of the water and gas energy is sufficient to lift the total volume of oil to the surface. The rate of production will decrease continually.

Capillary Control.

In a reservoir under "Capillary Control," though the water head H has created the potential energy in the gas above and associated with the oil, the resistance to its own and the oil's movement through the strata has been so great that the geological ages occupied in carrying out the work of compression would again be required to restore a balance should some of the energy be released from the reservoir.

Further, the energy stored in the free gas cannot cause bulk movement of the oil on the release of pressure in any one part of the reservoir.

If production of oil is to take place at all from a reservoir of this type, it must therefore be as a result of the expenditure of the energy of the gas dissolved and otherwise carried with the oil.

Herold's theory that production under these conditions is governed entirely by the laws affecting the movement of liquids and gases in capillary tubes is not entirely accepted by all physicists, but no other comprehensive theory has been propounded, and as its predictions fit in reasonably closely with the facts of actual production, it may represent the real conditions and has been taken as a working hypothesis in this paper.

If a tube of even capillary bore is filled with alternate globules of a liquid and bubbles of gas, it will be found that a considerably higher gas pressure has to be applied to one end of the tube to cause movement than would be the case if the tube were completely filled with either a liquid or a gas. It will also be found that the pressure required to cause movement to a chain of twelve such globules of liquid is exactly double that required to move a chain of six.

Somewhat similar results are obtained with a tube having a corrugated bore, but the pressure required to move a chain of globules is higher than that necessary with a plain bore tube.

There is a further difference between the two tubes in that it is necessary to introduce the globules into the plain tube one at a time, and if sufficient pressure is applied, the whole of the globules and bubbles of gas are expelled. With the corrugated tube however, if gas and water are fed in under pressure at one end, globules of water will form at the restrictions, and, if there is more water than is required to form the globules, the surplus will pass on from globule to globule until it is ejected at the end of the tube. If the water supply is cut off, the gas will continue to pass through the tube and displace the globules one after the other into the

larger portions of the tube. The globules will, however, reform after the passage of each bubble of gas, and none of the liquid forming the globules will be ejected from the tube.

A study of the gas pressures in each bubble in either tube will reveal that there is a progressive drop towards the orifice. This is easily understood as each globule gives a certain back pressure (f) so that the pressure in the bubble next to the orifice, if the orifice is discharging into atmosphere, is atmospheric pressure + f. The second bubble from the discharge end will be at atmospheric + 2 f pressure and so on.

Now consider an oil reservoir under capillary control. The spaces between the sand grains form capillary tubes of corrugated bore leading towards the well, the tubes being completely filled with oil having quantities of gas under pressure dissolved in it. As soon as the well is opened, the pressure at one end of the tubes is released and the gas expanding from the oil forces the nearby surplus oil into the well and forms chains of bubbles and oil globules stretching back into the sand. The bubble next to the well in the capillary tube is forced into the well by its own pressure and the pressure behind it, and its place is immediately taken by the bubble that was second from the well. In moving to its new position, the second bubble had to overcome the back pressure of one globule so that its pressure is less than the first by one f. Exactly the same action is going on at a distance from the well and continues, meantime passing surplus oil forward and into the well, until the pressure of the bubble in the space nearest the well being insufficient to overcome the back pressure of the well plus one f, movement ceases.

An examination of this final state will show that movement has only extended a certain definite distance from the well. If the back pressure at the well is p (it may be atmospheric or atmospheric plus a head of oil) the pressure in the bubble next the well will be p+f, that in the bubble second from the well p+2 f, and so on until at a certain distance n bubbles from the well p+nf equals the original pressure P in the reservoir. No oil or gas will have been produced from beyond this distance, and the contents of the reservoir will, beyond this distance from the well, be in exactly the same condition as they were before the well was drilled, nor will their condition change as a result of the one well, no matter how long a time may elapse.

It has been assumed here, merely for facility of presentation, that an oil reservoir consists of a definite number of capillary tubes leading towards the well. Obviously, in practice, the number must increase as the distance from the well increases. If there is one tube at radius R there will be two tubes at radius 2 R and so on. the complete arrangement being as shown diagrammatically in Fig. 2.

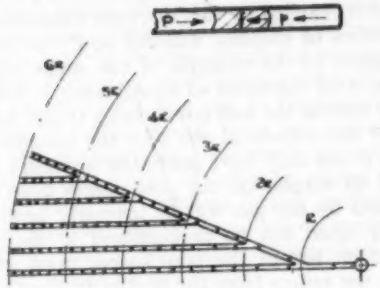


FIG. 2.

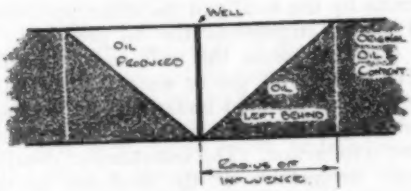
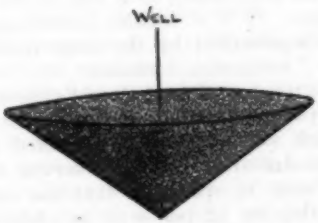


FIG. 3.



VOLUME CONE

FIG. 4.

It will be seen however that the number of f's in any one line to the well is not changed by this sideways extension ; the formula for final conditions of stability will still be $P=p+nf$.

Reverting again to the example of the single capillary tube to the well in the final condition of equilibrium, it will be clear that the gas bubble nearest the well must, owing to the reduced pressure, be many times the volume of one near the boundary of the well's influence, and it can only have made the necessary space for itself by clearing of all surplus oil the pore spaces near the well. The volume occupied by the gas will be inversely proportional to the pressure which again will be proportional to the radius, so that the amount of oil left in the pore spaces must increase proportionately with the radius from the well until the limit of influence of the well is reached.

The density of distribution of the surplus oil in the sand when production ceases gradually increases from nothing at the well to the original density at the edge of influence of the well, and may be represented by a diagram. (Fig. 3.)

The density of distribution, when production ceases, represents oil unrecoverable by the well, and the difference between the final and original density represents the oil produced. This is the same in all directions from the well, and, therefore, to quote Herold : " The isolated oil, gas or water well in capillary control produces one-third of the fluid underlying its drainage area, such fluid being mobile at the given constant back pressure which is exerted against production. The quantitative distribution of this produced fluid, irrespective of the thickness of the formation which serves as a reservoir, may be represented by a space diagram in the form of a right circular cone with a base of radius R." (Fig. 4.)

The term " mobile oil " is here used in the same sense that " surplus oil " has been used previously. It excludes all oil which is adsorbed by the pore spaces or is held in the restrictions of the capillary passages. It is a smaller percentage of the total oil content than is represented by the same term when applied to " hydraulic " or " volumetric " control.

That, then, is a rough outline of Herold's theory of the mechanics of oil and gas production from a single well under " capillary control." As each well affects only a limited area, a number of wells have to be drilled to drain a reservoir and Herold shows that such wells must be spaced so that the radii of their circles of influence overlap by 12 per cent. to obtain one-third of the total mobile contents of the reservoir and that production of all the mobile oil could be obtained only by wells drilled all over the area with their casings touching.

He shows that where circles of influences interfere the vertical plane through their points of interference is a neutral plane and that no oil on one side of this plane can be produced at the well on the other side. Wells having interfering circles of influence produce only that portion of their volume cones lying inside the neutral plane. For two wells this can be illustrated as Fig. 5.

With a number of closely-spaced wells the volume cone is cut on all sides by the neutral planes and wells spaced as shown on the plan, Fig. 6, having circles of influence whose radii interfere by 142 per cent., would have volume figures as shown on Fig. 7. It will be noticed that drainage of the mobile oil would theoretically be almost complete, that small portion between the conical points alone representing mobile oil left behind.

He then proceeds to show that, by pumping back a liquid or a gas into one of a group of wells whose radii interfere by less than 100 per cent., the pressure in the reservoir surrounding the input well can be restored to the original pressure of the reservoir, and the effect of its interference may thus be negatived so that the other wells produce as if it had not been drilled and some of the otherwise unobtainable oil is produced.

He then shows that, by further increasing the pressure, a point can be reached when the resistance of the chain of bubbles and globules between the input and its surrounding wells is overcome and a fluid drive is set up which, by a further increase in pressure may be made to influence increasingly large areas of elliptical shape between and surrounding input and output wells, until theoretically the whole of the mobile oil is produced.

The full thesis, containing 517 pages and 631 numbered formulæ, obviously cannot be completely dealt with in the few sentences possible to devote to it in this paper. Sufficient has perhaps been said to bring out its salient points, and members interested will no doubt study the work itself, if they have not already done so.

Practical Application.

It must again be emphasised that Herold's theories are based on perfect substances and conditions.

In practice a reservoir under "hydraulic control" would behave exactly as his theory predicts, no matter how it was drilled up or produced. If there were certain knowledge that "hydraulic control" existed, and would continue until all oil was produced, a ring of wells just sufficient to give the required oil production would be drilled just below the gas/oil boundary and, when all the wells had turned to water, others would be drilled in the top of the dome to obtain the gas. If quantities of gas were required in the early states of the development of the field, the dome wells could be

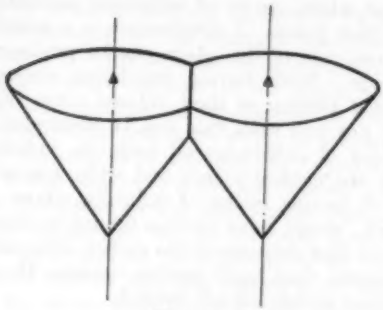


FIG. 5.

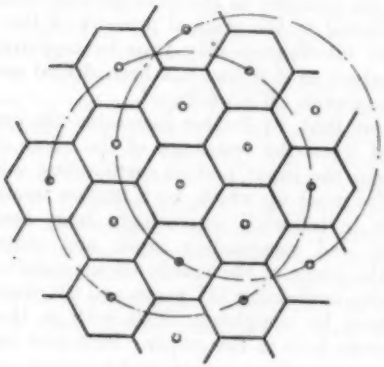


FIG. 6.

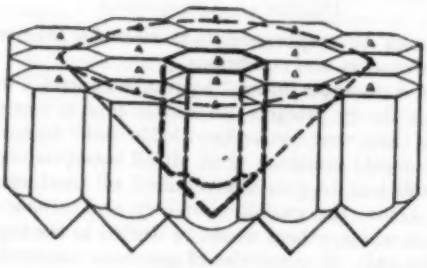


FIG. 7.

drilled earlier without materially affecting either the rate of production or the ultimate quantity of oil produced which, in any case, would be the total oil content of the reservoir, excluding oil originally adsorbed by the pore walls in the reservoir. Gas has no essential part in the production of oil from a reservoir under "hydraulic control," and may be produced in any quantities or not produced to suit circumstances.

Under "volumteric control," water under a head or gas under pressure, or both together, may be the source of energy for moving the oil through the reservoir. In the first case no gas is present with the oil, and production will take place exactly in accordance with theory; but in the second and third cases, gas provides half of the energy available, and, if it is allowed to escape without doing its quota of work in moving oil to the well, the whole of the mobile oil may not be obtained. The retention of all the gas in the dome, and the drilling of a ring of producing wells on the line at which water and gas will meet when all mobile oil is produced, would be the most economical way of draining the reservoir. Unless the potential energy of the gas and water is much in excess of that required for complete oil production, restriction of gas production at each well to as near as possible the amount actually carried in solution or as liquefied gas by each volume of oil at the particular pressure of the reservoir will be essential; in other words, by-passing of gas must be restricted and the rate of production must be controlled by beaning to this end.

If there is sufficient potential energy in the gas or gas and water for complete production, then the return of surplus produced gas to the dome will be simply waste of money. The return of stripped gas would keep up the dome pressure and increase the possible rate of production, but generally the same effect could be obtained, if desired, by reducing the back pressure against the exposed reservoir surface in the well, either by increasing the size of the bean at the well head, or, if that were insufficient, by reducing the oil head in the well by mechanical lifting of the oil or further by imposing a vacuum. The return of stripped gas to the dome would affect, to a certain extent, the quality of the oil produced as, at the higher pressure, less of the lighter fractions would be vaporised and left behind for production after oil production had ceased. The cash value of the accelerated production of these lighter fractions might more than pay the amortisation and running costs of the necessary plant, but there is a considerable element of doubt as to this and each individual case would have to be very carefully scrutinised before a repressuring or gas return scheme were adopted in a reservoir under "volumetric control."

It is, of course, always possible that a reservoir under "volumetric control" at the beginning of its life might change to "capillary control" before complete oil production is obtained, either because the quantity of original potential energy was insufficient or because energy had been wasted. In such a case, repressuring would be well worth while as, by restoring the reservoir to "volumetric control" all the mobile oil could be produced, whereas, if left under "capillary control," many more wells would be required, and much of the oil content would be left behind, even although the most complete gas drive possible were carried out. In any case, gas driving would probably be not less costly than repressuring, and its cost would come in the declining years of the field when flowing had ceased and lifting costs were being incurred. If, therefore, there seems any chance of a reservoir changing from "volumetric" to "capillary control," repressuring in the early stages of production to prevent the change, or at least to delay it, would seem advisable.

It is, of course, impossible to discover the form of control existing in any reservoir until production has continued for some time, and even then, if new wells are continually being opened up, "hydraulic control" may not easily be distinguished from "volumetric." A reservoir under "capillary control" can be recognised by the absence of interference between closely spaced wells, but the presence of interference over considerable distances and even a lowering of the reservoir pressure with production, is no certain indication that the reservoir is under "volumetric" and not "capillary control."

To be on the safe side, it is always advisable to assume the more complex condition, and to produce accordingly until definite proof of the existence of the simpler condition can be obtained.

In reservoirs under "capillary control," it is clear from what has already been said that every possible effort must be made to utilise to the full every foot pound of available gas energy. Each volume of oil has originally with it a certain volume of gas; the oil itself has only the potential energy imparted to it by gravity, and is of itself practically immobile. The gas with the oil is charged with energy sufficient to move through a certain distance not only itself, but its associated volume of oil towards the well. In the theoretical considerations, it has been assumed that each volume of gas acts on its associated oil right from the commencement of movement until either both are produced or a condition of equilibrium is reached. In practice, much of the gas will not act in this perfect manner, but will spend its energy producing itself at a faster rate, leaving much of the theoretically producible oil as "dead" oil in the reservoir.

The volume cone of production of a single well would then be converted to a figure as shown in Fig. 8, and for interfering wells as Fig. 15.

The "dead" oil is, of course, only "dead" relative to the particular producing system under consideration. It might be "live" relative to another producing system, such as a second well drilled subsequently within the circle of influence of the first, but its "liveliness" would be less than that of the oil originally in the reservoir, and the second well would consequently have a smaller circle of influence than the first.

With perfect action throughout on the part of the gas, production of gas and oil at the well would throughout the life of the well be in the ratio in which they originally existed together in the

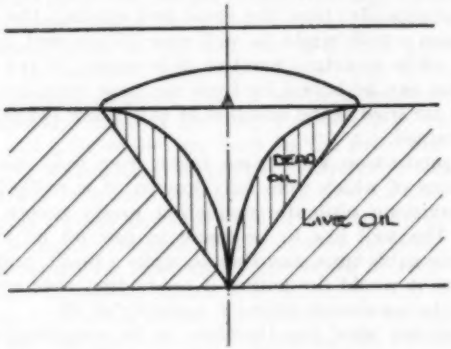


FIG. 8.

undisturbed reservoir, and the aim of all producing methods must therefore be to produce at as near the original gas/oil ratio as practical and economical considerations will allow.

The only place at which control can be exercised is the well itself, and that control can take the form only of varying the oil head or gas pressure on the reservoir face. Both can be varied together or independently, and there is consequently an infinite variety in the form of control which can be imposed.

Before discussing possible control measures, it will be well to clear the mind of ideas of perfect production of perfect liquids and gases from perfect reservoirs, and to try and visualise conditions more nearly approaching those actually found in oilfields.

The physical properties of gas and oil, together and separately, vary enormously with changes in pressure, temperature and the relation of their associated quantities. The viscosity, surface

tension, specific gravity of the oil, all of which have an effect on the mobility of the oil, change during production. The strata of oil reservoirs are not homogeneous, neither is the gas and oil evenly dispersed throughout them. Further, it seldom happens that one reservoir only is producing into each well, as economic considerations necessitate that each well shall serve as an outlet for the oil and gas from groups of reservoirs of frequently a total thickness of many hundreds of feet. Each reservoir may be divided from its neighbour by only a few feet, or even inches, of impervious strata, but the original conditions in each cannot be relied on to be, and seldom are, exactly similar, though possiby all are of the same order. It must further be realised that the radius of influence of any one well is probably several times the usual spacing distance between wells, even where offsetting has not been the controlling factor. Theoretically, from the usual well spacing, the percentage recovery from a field might be well over 75 per cent. of the total mobile oil, while in actual practice it is nearer 25 per cent., and the best that can be hoped for from the most scientific producing methods so far tried is the addition of only a few per cent. to that already obtained.

Even if production were being taken from only one reservoir, the conditions of which were fully known, it is unlikely that the ideal of maximum ultimate production would govern producing methods. The well has to be made to pay off its capital cost within a reasonable time, and then to make a profit, and it is quite possible that it would do neither if production were controlled so as to give the maximum ultimate quantity of oil.

The producing ideal has therefore to be something of a compromise between taking oil at the possible maximum rate, irrespective of gas/oil ratio, and taking oil at the rate at which it can be produced at the reservoir gas/oil ratio. A number of wells in a field should be tested under as many different producing conditions as possible. If a flowing well, it should be flowed as nearly full open through its casing as is considered safe, and should be gradually choked back, taking careful note of the rate of production and corresponding gas/oil ratio for each condition. A flow string or tubing, preferably with a bell nipple on the bottom, should then be inserted to varying depths, and details of production and gas/oil ratio should be taken at each depth of flow string or tubing, with the casing head closed and with it open by varying amounts to give varying back pressures, and with the flow string or tubing full open, or beaned down to give varying back pressures against flow through it. Different sizes of flow strings should also be tried under similar varying conditions. On wells which have ceased to flow, experiments with different methods of oil lifting, gas lift,

gas pumps and ordinary pumps with varying back pressures on the casing head, different depths of tubing and rates of production should also be made and all possible information obtained for each condition.

Careful scrutiny of all the data obtained will show that the gas/oil ratio varies on each well as the conditions are varied, and it should be possible to find an optimum producing condition under which a maximum quantity of oil is obtained with a minimum quantity of gas at each stage in a well's life in any one field. Production under these conditions should result in maximum ultimate production from the field, and if economic considerations will allow they should be adhered to.

The lowering of the rate of production per well which results from working under the optimum condition will, of course, put up the capital cost of production if the overhead production of the field is to be maintained, as the well cost is a fixed amount and the amount of oil produced from the well per day is less. In other words, to maintain a given daily production, more wells will have to be drilled and more of the money obtained by the sale of the products will have to be put back in the field, and less will be available for distribution as profits. Obviously, there is a limit to the amount of money that can be spent on a field for the sake of prolonging its life, as unless running expenses, plus amortisation of and a reasonably interest on the money invested, can be met operations cannot be continued. The effect of such a restriction of production to prolong the life of a field on the cost of maintaining a barrel/day of production now, has therefore to be balanced against the results of less restriction but a shorter life. Needless to say, such a balancing up of such indefinite and continually changing quantities and values, if possible at all, can only be in a very rough way, and it may be possible merely to lay down as a working rule some such principle as the following :—

> If a modification of producing conditions can be made so that a 50 per cent. reduction in gas production is accompanied by not more than a 10 per cent. reduction in oil production, it is worth while carrying out.

The difficulty of the whole problem can be no excuse for neglecting consideration of it. The cost of experiments and the examination of the data obtained will not add materially to the cost per barrel of oil produced in the early stages of a field when oil may be relatively cheaply won, and the information obtained, if used to the best advantage, should not only result in a lowering of crude costs in the declining years of the field, but should also result in increasing the number of years during which oil can be produced at a profit.

Repressuring—Theory.

If, after completion of production from a single well down to a given back pressure under "capillary control" gas is injected into the well until the pressure at the well equals the original reservoir pressure, then the pressure conditions throughout the circle of influence of that well will be as they were originally. If the well is then opened to the original back pressure, the gas

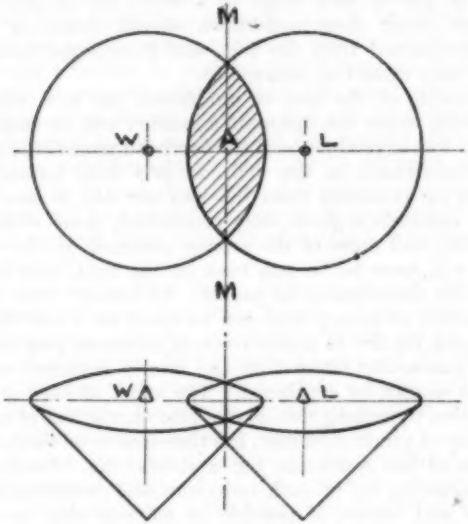


Fig. 9.

will be produced again under "capillary control," but it will not bring with it any of the oil which was left behind during the original production.

Where there are two interfering wells under "capillary control" Herold shows that, by repressuring, the effect of interference can be nullified, and each well will produce the amount which it would have produced had the other not been drilled.

Consider two wells W and L whose radii of influence at a given back pressure interfere by 66·6 per cent. (Fig. 9).

Assume W drilled in first and produced to exhaustion, the quantity of oil obtained from it being represented by a cone, and that left behind by a density diagram which is a section through the cylinder of influence. If now W is repressured to its original pressure,

The distribution of oil in the density cylinder will be changed and may be represented by a hollow cylinder with walls of a thickness equal to 0·423 times the radius, the centre cylinder being filled with gas, Fig. 10. When the second well, L, is drilled in it will produce its normal volume cone of oil just as if the first well had not been drilled. It will be seen that twice the quantity of oil which would normally be obtained from the area A is obtained if well W is first produced then repressured, and well L is then produced.

If both W and L were originally produced together, each would obtain a portion only of the oil due to it from the area A, as no oil from one side of the neutral line M–M joining the points of

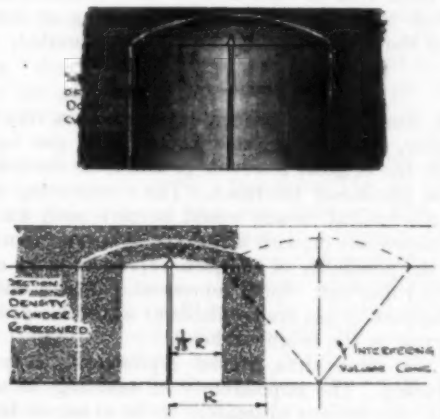


FIG. 10.

intersection of the circles can be produced at the well on the other side. On repressuring W to its original pressure, the neutral line will disappear and the oil which was held back from W by L will be produced together with an amount to make up the normal production of L under conditions of no interference. Repressuring therefore results in twice the volume of oil, represented by the interference of the volume cones, being produced instead of once the volume with ordinary unassisted production.

It has already been indicated that, in practice, the full volume cone of oil will not be produced, but much of the oil will be left behind robbed of some of its gas (Fig. 8). Repressuring will only partially revivify this oil and consequently it will have to be moved much closer to the neighbouring well before it will come within

its circle of influence. To obtain the quantity of oil theoretically producible by repressuring would therefore require a higher pressure than the original reservoir pressure.

It is easy to see that the effect of repressuring of a field which has previously been drained as completely as possible by wells whose radii of influence interfere by over 100 per cent—as in ordinary practice—is extremely difficult to estimate. All but the few input wells would have to be closed in until the pressure was restored, and when opened up some would produce only gas and others gas and oil, possibly much as they had done originally. All the wells would, however, produce only a definite proportion—depending on their spacing of the oil and gas content of the sand within their area of influence, so that it seems safe to say that even with the most complete repressuring or several such operations, all the mobile oil would not be produced.

Repressuring—Practice.

In practice, complete repressuring is, except in a very few cases, an impossibility, as it necessitates a volume of gas equal, when compressed to the original reservoir pressure, to the total volume of oil and gas previously produced. The compressing of such an amount by mechanical means would involve such an enormous number of compressors or, with a reasonable number, such a length of time that the possibility of complete repressuring by mechanical means can be ruled out. Such repressuring is a possibility only when large supplies of gas are available at a suitable pressure from another reservoir in the neighbourhood.

Generally not more than partial repressuring is possible by mechanical means. The impossibility of assessing, at the time it is carried out, the returns ultimately to be obtained from partial repressuring makes it impossible to say whether the procedure will or will not pay. The only principle that can be worked to is that all gas returned to the sands will in time have some good effect on production, and it is better therefore to return surplus gas to the sands than blow it to atmosphere, which in many cases is the only alternative, provided it can be done without a large expenditure of capital specially for the purpose, *i.e.*, if the necessary compression can be made incidental to gasoline extraction.

Gas Drive—Theory.

In a reservoir under "capillary control," if gas is injected into one well at such a pressure as will overcome the resistance of the chain of bubbles and globules between it and a neighbouring well, a gas drive will be started and all the mobile oil on the vertical line joining the two wells will be produced into the output well.

If the pressure is then further increased, portions of the reservoir on either side of this line will come within the influence of the gas drive, and oil in them will be driven forward along radial lines from the input well. Provided that the oil is active or, in other words, has with it some of its original gas energy, it will, though not forced in a straight line to the well, by the gas drive, come within a circle of influence of the output well proportional in size to the energy content of the oil, and will be produced into it. Oil, however, which is "dead" in relation to the output well, will make no effort to get into that well but will continue on its radial path past the well until the pressure behind it is released by production of the gas drive gas in the output well. Even if a number of output wells surround the input well, only a very small percentage of the oil within the circle will be produced, and much of the energy of the compressed gas used in the drive will be consumed in moving "dead" oil from one part of the sand to another, and in passing the gas straight through from the input to the output well without its doing any work whatsoever in producing oil (Fig. 11).

Better results would be expected from a gas drive, whether acting on "dead" or "live" oil, by a line drive, Fig. 12, as each output well would be receiving oil from two directions with a consequent congestion at the well which would to a certain extent prevent bypassing and allow the building up of pressure over a wider area. With "dead" oil, a triangular area between the input wells and the output well would be affected instead of little more than the plane joining the two (Fig. 13).

Better still, the author believes, would be centripetal drive, where a number of input wells drive into one central well (Fig. 14). In this scheme the congestion at the well would be greater still and bypassing would be hindered to a greater extent, consequently higher pressures could be built up at the input well and greater areas affected.

With a whole field covered with systems such as this, it is possible that very large quantities of what is considered at present as irrecoverable oil might be obtained with possibly a smaller quantity of input gas than is now being used for "centrifugal" or "line" drives.

Gas Drive—Practice.

The small profit usually obtained from gas drives of the "centrifugal" or "line" type makes accurate accounting of costs incurred and values obtained essential. Quantities of gas are left below in the process and, as it is unlikely that they have any considerable revivifying effect on the oil, the best that can be hoped is that they will be reproduced in their original volume, possibly

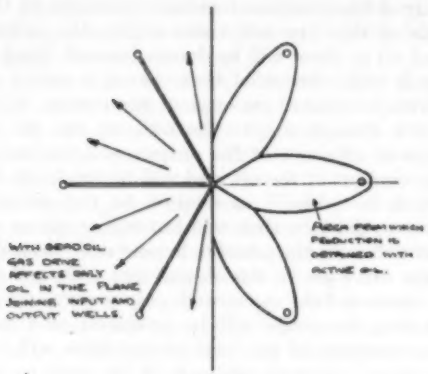

WITH DEAD OIL GAS DRIVE EFFECTS ONLY OIL IN THE PLANE JOINING INPUT AND OUTPUT WELLS
AREA FROM WHICH PRODUCTION IS OBTAINED WITH ACTIVE OIL.

FIG. 11.

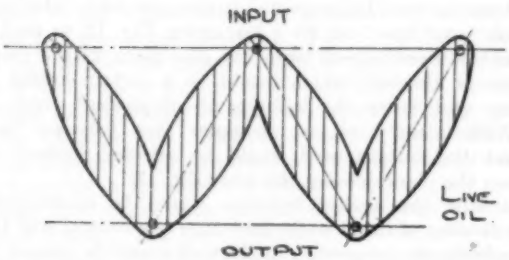


FIG. 12.

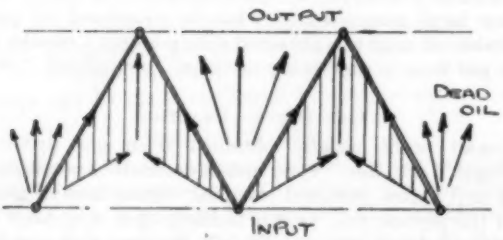


FIG. 13.

enriched with gasoline vapours at a later date, when the gas drive pressure is released. Meantime, if the gas has any sale value or value as fuel, such value has to be debited to the gas drive cost. The value of the fuel consumed in the compressors, which may be as much as 10 per cent. of the volume handled, is a further debit, as also are the running cost and amortisation charges of the compressors. On the credit side can be placed only the value of oil

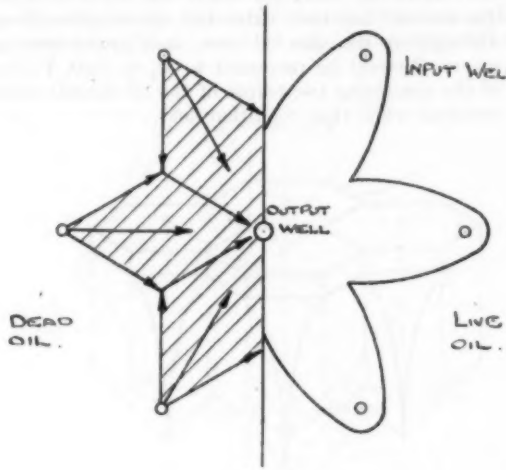


FIG. 14.

which would not otherwise have been won during the normal operating life of the field. The small additional value of oil won now, as against oil won in two or three years' time, will seldom balance the operating and other costs of a gas drive, and it is necessary to make reasonably sure that only the value of oil which would not otherwise be won is the credit given to the operation.

CENTRIPETAL PRODUCTION—THEORY.

The centripetal gas drive, already suggested, was as a means of obtaining more oil from a reservoir from which the utmost production had already been won by normal methods at normal well spacings. It is possible, theoretically at least, to apply the same ideas to virgin production by employing injected gas to displace the oil from the commencement of the producing operation. To avoid the use of the words " gas drive " or " repressuring," neither of which describes properly the function of the injected gas, the scheme has been given the name " centripetal production."

As previously shown, a single producing well in "capillary control" obtains its production from a certain limited area covered by its circle of influence. The size of the circle is governed by the back pressure at the well, p, the pressure of the gas associated with the oil, P, and the resistance of the bubbles and globules in the capillary passages, nf, so that $P=p+nf$.

The amount of production obtainable is one-third of the total mobile oil content of the reservoir inside the circle of influence, and when this amount has been extracted, the relation $P=p+nf$ holds true throughout the affected area, and production ceases. If by any means P could be increased to P_1 so that $P_1>p+nf$, movement of the remaining two-thirds of the oil would commence and would continue while that condition held

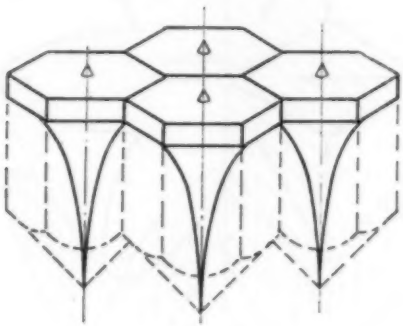


FIG. 15.

An increase in pressure at the periphery of the circle of influence can be obtained by surrounding the producing well with wells solely for gas injection purposes, drilled with their casings touching on the circumference and by injection into them of gas at a pressure equal to, or slightly higher than, the original reservoir pressure.

The injected gas would work forward towards the producing well under the laws of "capillary control," but, in doing so, would carry before it to the well the whole of the mobile oil within the circle.

A complete reservoir could be dealt with in this way by drilling output wells on the triangular plan, so that the radii of their circles of influence interfered by 26·8 per cent., and surrounding them with gas injection wells drilled on the neutral planes joining the points of contact of the interfering circles. Production of all mobile oil in a reservoir would ensue.

It will be noted that whereas, with ordinary producing methods, complete production could be obtained only by drilling all over the field wells whose casings touched, in this scheme rings of such wells only would be required surrounding a few output wells.

The presence of "dead" or "vitiated" oil in the system, caused by bypassing during production of the gas originally with the oil, would make no difference to the ultimate recovery, though higher pressures would be needed at the injection wells.

The quantity of gas left in the reservoir after completion of oil production would be the amount required at the original reservoir

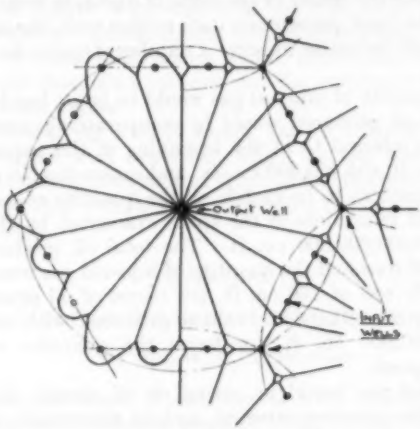


FIG. 16.

pressure to fill with gas, two-thirds of the pore space from which oil had been evacuated. A portion of the gas could, however, be produced by converting the gas injection wells to producing wells.

CENTRIPETAL PRODUCTION—PRACTICE.

It is obviously impracticable to drill injection wells with their casings touching, but if the usual well spacing gives an interference of 142 per cent. of influence circle radii, as is probably the case on most sand fields, a very reasonable surround of injection wells can be drilled, Fig. 16, without increasing the total number of wells on the field. More injection wells might be drilled without increasing the total drilling cost above that necessitated by the more usual producing methods as, being mainly for gas injection or gas production, the wells could be small in bore and cheaply drilled.

Production of all mobile oil would not be obtained at the centre output well, but the small quantity of oil remaining would be

between the injection wells, and most of it would be produced from them after production from the centre well had ceased.

As some injection wells are slightly closer to the output well than others, a slight variation in injection pressure would be necessary. Similar variations would be necessary to compensate for tight and loose patches in the reservoir.

Where it is necessary to deal with a number of reservoirs with the one series of injection wells, the difficulties which might be caused by their different conditions of porosity, pressure, etc., could be overcome by drilling a separate output well for each reservoir as near the centre of the circle of injection wells as possible. By varying the back pressure on each output well, the one injection condition could be made to serve a number of reservoirs reasonably efficiently.

The total quatity of injected gas would be large, but the quantity per barrel of oil produced would be comparatively small. In the assumed field referred to at the beginning of the paper, the total oil space was 10,454,400,000 cu. ft. and, assuming 75 per cent. of the total oil content to be mobile oil the quantity of gas at N.T.P. required to fill two-thirds of the space evacuated by the oil would be about 179,000,000,000 cu. ft. The total oil production would be 174,500,000 tons and the quantity of injected gas would therefore be 1035 cu. ft./ton or 150 cu. ft. per barrel of oil produced. The total quantity of methane and ethane produced with the oil would be 367,000,000,000 cu. ft., or twice the quantity required for injection purposes.

The injected gas would be acting on oil already fully charged with gas at the injection pressure, and no absorption of gas would therefore take place. There would be no advantage in using wet gas, in fact air might be used with greater advantage than gas. There might, however, be bypassing in the later stages of production, when the air gas mixture produced from the wells might be a danger. Bypassing should not however be extensive as the production of the injected gas would be governed by "capillary control."

Production from the output well would take place at a steadily decreasing rate, and would be completed in a reasonable time from the point of view of the usual duration of concessions. The rate of production could be speeded up by increasing injection pressures and quantities. The scheme does not necessitate the drilling up of the whole field at one time, but if produced in units each would have to remain charged with gas or air until neighbouring units were produced.

The scheme, unfortunately, so far only a paper one, offers the possibility of doubling or trebling the total quantity of oil obtainable

from sand or tight limestone fields without a departure from ordinary oil field practices such as its only rival, oil mining, demands; it offers separate production with one series of wells from each of a number of sands whose properties may vary to almost any extent; it offers a rate of production that can be regulated within wide limits to suit circumstances and complete drainage within time limits such as can be visualised and allowed for in an ordinary commercial undertaking. Its capital and development costs should be no higher than those necessitated by present methods, and its oil producing cost should, if anything, be less. It gives, in fact, such a river of promise that the instinctive feeling is for a snag somewhere. However, the risk of experiment seems, to the author, to be worth while taking, and he hopes that some producing company will share his views and put the scheme to the test in the not too-distant future.

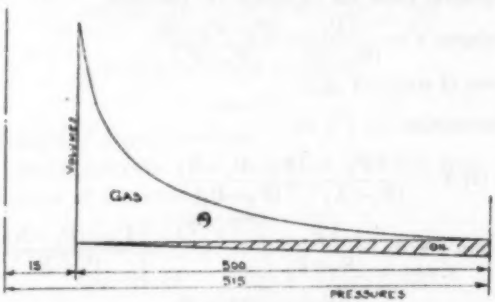
In conclusion, the author would like to acknowledge the very helpful criticism and assistance which he has had from Messrs. Jackson, Abraham, Bowles and Wade of the Burmah Oil Company, and to thank that company for permission to place the Paper before the Institution.

Appendix I.

Potential Energy of Dissolved Gases.

By Mr. W. C. A. Bowles.

A gas, say methane, is compressed from absolute pressure of 15 lb. per sq. in. to absolute pressure of 515 lb. per sq. in. It obeys Henry's law and at the latter pressure is entirely absorbed into the oil. Required, the work done in compressing the gas.

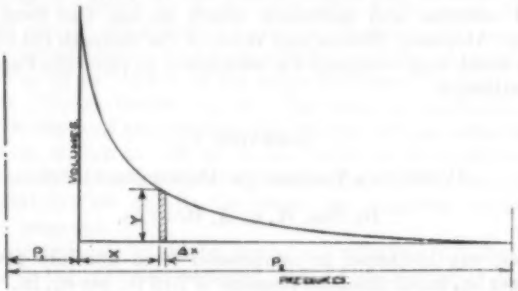


The volume at 15 lb. pressure is V.

Assuming that at 16 lb. pressure no oil has been formed, then the new volume would be $\frac{V \times 15}{16}$ (Boyle's law). But oil has formed and is equal to $\frac{16-15}{515-15} = \frac{1}{500}$ the original quantity of gas. Deduct this quantity and we have a volume $\frac{V \times 15}{16} \times \frac{499}{500}$ gas remaining.

Similarly, at a pressure of 17 lb. we have volume gas remaining $= \left(\frac{V \times 15}{16} \times \frac{499}{500}\right) \frac{16}{17} \times \frac{498}{499}$ This, of course, can be proved by taking a step of 2 lb. thus.—

(1) $\frac{V \times 15}{17} \times \frac{498}{500}$ which is equal to previous quantity.



V=Volume at atmos. pressure. P_1=atmos. pressure abs. P_2=final pressure abs.

In a general form the equation (1) becomes

(2) Volume $Y = \frac{VP_1}{(P_1+X)} \frac{(P_2-P_1-X)}{(P_2-P_1)}$

Area of strip $= Y.\Delta X$

Summation $= \int Y.dx$

From (2) $Y = \frac{VP_1}{(P_1+X)} \frac{(P_2-P_1-X)}{(P_2-P_1)}$

Therefore $\int Y.dx = \frac{VP_1}{P_2-P_1} \int_0^{P_2-P_1} \left\{\frac{P_2-(P_1+X)}{P_1+X}\right\} dx$

$= \frac{VP_1}{P_2-P_1} \int_0^{P_2-P_1} \left\{\frac{P_2}{P_1+X} - 1\right\} dx$

$$\text{Area} = \frac{VP_1}{P_2-P_1}\Big[P_2\log_e(P_1+X)-X\Big]_0^{P_2-P_1}$$

$$=\frac{VP_1}{P_2-P_1}\left\{P_2\log_e(P_1+P_2-P_1)-(P_2-P_1)-P_2\log_e(P_1+0)+0\right\}$$

$$=\frac{VP_1}{P_2-P_1}\left\{P_2\log_e P_2-(P_2-P_1)-P_2\log_e P_1\right\}$$

$$=\frac{VP_1}{P_2-P_1}\left\{P_2\log_e\frac{P_2}{P_1}-(P_2-P_1)\right\}$$

Taking V as 1, P_2 as 515 and P_1 as 15 we obtain

$$=\frac{15}{500}(515\times3{\cdot}53614-500)$$

$$=\frac{15}{500}(1821{\cdot}112-500)$$

$$\frac{15}{500}\times\frac{1321{\cdot}112}{1}$$

$$=39{\cdot}63336$$

METHANE.

The work done in compressing one cubic foot of methane or ethane gas from 15 lb. per sq. in. absolute to 515 lb. pet sq. in. absolute.

$$=39{\cdot}63336\times144 \text{ ft. lb.}$$

Total volume of dissolved methane

$$=10{,}454{,}400{,}000\times0{\cdot}07=731{,}808{,}000 \text{ cubic feet.}$$

Total volume of methane gas at N.T.P.

$$=731{,}808{,}000\times620 \text{ cubic feet.}$$

Energy required to compress or expended in expanding

$$=\frac{731{,}808{,}000\times620\times39{\cdot}63336\times144}{2240\times233{,}357{,}000}$$

$$=4954 \text{ ft. tons per ton of oil.}$$

ETHANE.

Total volume of dissolved ethane

$$=10{,}454{,}400{,}000\times0{\cdot}01=104{,}544{,}000 \text{ cubic feet.}$$

Total volume of methane gas at N.T.P.

$$=104{,}544{,}000\times355.$$

Energy required to compress or expended in expanding

$$=\frac{104{,}544{,}000\times355\times39{\cdot}63336\times144}{2240\times233{,}357{,}000}$$

$$=405 \text{ ft. tons per ton of oil.}$$

DISCUSSION.

The President remarked that Mr. Ellis's paper had been a most illuminating discourse on what—for want of a better term—might be called the geometry of a producing field. The question was obviously of the greatest importance at the present moment, when over-production was throwing a shadow over the whole industry. Only a fortnight ago, in Chicago, all the brains of American oil producers had been directed towards solving this great problem of the relationship between the production of oil and gas; it had been put forward as a solution of the present difficulties in the industry that the production of gas *qua* gas might well come within the scope of the ordinary State legislation. As a chemist, he did not feel entitled to discuss so intricate a matter, but would call upon Professor Lilley, of the University of New York, whom they had the honour to welcome that evening, to make himself known to the Institution in person and to favour them with his views.

Professor E. R. Lilley stated that he had attempted at various times to read Stanley Herold's theories. He had found that after one passed the tenth page one did not know what had been on the second. He had nevertheless taken heart and managed to acquire some knowledge of them.

Mr. Ellis had suggested a system of drilling new air or gas-pressure wells. He, himself, had no fault to find with the system, but pointed out that before the first barrel of oil was secured the complete ring must be finished, and that the initial investment was therefore rather high. In the long run it might be possible to produce a considerable amount of oil from the horizon that would not have been secured by the ordinary system, but the first cost was a very serious item. An investigation into the history of the air-drive and the water-drive, as illustrated by the Bradford section in Pennsylvania and New York States, showed that it was not always the large company that started operations in such sections, but frequently the small company or individual. The individual, to whom the cost of drilling even two or three shallow wells was a serious item, would probably become bankrupt if he attempted to operate on a system which called for the immediate drilling of a large number of wells. Moreover, before the small producer had completed the circle of air-wells, the price of oil might have dropped so materially that the returns would not be commensurate with the investment.

Some of the companies that had started operations in the Bradford section had made substantial amounts of money. This section is the great centre of Pennsylvania grade production to-day. The oil is of high quality, and was worth $6.10 per barrel shortly after the War. Three years ago several companies were making large

profits from flooding operations with very modest outlays. Others rushed in to share in the profits. Now oil is being produced in such quantities that the market is not able to absorb it all. The price is only a little above one quarter of that immediately after the War.

The President, he said, had also mentioned the use of State legislation to assist in the control of the oilfields through the regulation of gas. In the United States, the State was the supreme power as far as operations within its borders were concerned. The Americans believed to the utmost in property rights; private property was put first and Government regulation almost last. Unless there appeared to be some interference in industry and commerce, the central Government could do very little to regulate industry. Mr. Henry L. Doherty had attempted to secure Government aid through the use of the "War Power" of the Government, which allows it almost unlimited powers. There were, however, few lawyers who agreed with him in the use of that means. The State had the general power to protect the public welfare, and also power to protect the private individual, and it was difficult to define exactly where those powers began and ended. It seemed, however, that, either on the ground of public interest or on the ground of private right, the State had the power to prevent waste. This power had been used to prevent the burning of gas in the atmosphere, and had in some States been applied to prevent the use of natural gas in the making of carbon black. The decisions in the courts were not all in strict harmony; some were for and some were against.

The oil industry, having got itself into difficulties by drilling too many wells, was trying to induce the States to apply this rule, on the basis that if gas were allowed to waste (and the same was true of oil) into the air, or was sold at a very low price, waste was committed, either against private individuals or against the State, and should be prohibited. In other words, the State had the right—a part of the industry contended—to regulate the production and the usage of gas, and through that regulation to stop oil from coming to the surface. This provision would probably reach the statute books. Personally, Professor Lilley said, he disliked interference by the Government with business (applause). This type of regulation, however, was likely to become law in various States, and at present the courts would probably uphold the laws in the interest of the people in general.

The next step would, he said, be the building of more pipe-lines to carry the gas to distant markets, so that no matter how much gas was produced there would be a market for it. Regarding direct prohibition or restriction by law of the production of oil during periods such as the present nothing definite could be said.

Prof. V. C. Illing said the subject of this evening's paper was one of great importance to the industry and he congratulated the author on the clear and concise exposition of Herold's conceptions. These conceptions were based on certain assumptions and, while the speaker did not wish to decry the value of the general formulæ, he suggested that in some respects the ideas put forward by Mr. Herold required modification. Mathematical conceptions depended very much on the data which are utilized in the broad generalizations. When dealing with the phenomena of movement of oil through sands it was essential to know something of the properties of those sands. The speaker's main criticism was that the effects of variation in lithology overshadowed all else and vitiated many of the broad conclusions. He submitted that there was no such thing as a homogeneous stratum, even allowing that all the grains in a mass of sand were of the same dimensions (a condition which never applied), none of the grains was spherical. When these grains fell into position to form a stratum they lay with their longer diameters horizontal or slightly inclined. This meant that the passage of liquids parallel to the bedding was always very different from that athwart the bedding, and the inclusion of thin laminæ of fine material or alternatively the presence of joints or fracture planes played a very important part in the determination of the lines of drainage. The speaker was not so much criticising the use of mathematics, as indicating the presence of other factors which in his opinion played a large part in determining oil and gas drainage.

With regard to volumetric, hydraulic and capillary control he thought that it was exceptional to find any of these present alone in an oilfield, though volumetric control seemed to be more commonly present than any of the others. He was not at all certain about the condition of capillary control. The analogy that Mr. Ellis had used, of fine capillary tubes, was not truly comparable to the capillaries in sands. It was necessary to realize that in uncemented sands the capillaries were not a series of tubes, but one complex chamber partially filled with solid particles—the sand grains. The result was an infinite possibility for capillary by-passing. The oil became locked away near the contact of the grains, while the gas made use of the broader chambers through which it could pass without hindrance. When, therefore, some of the gas had come out of solution and had driven the quota of oil to the producing well there arose a condition wherein the remaining gas could pass through the partially drained sand without any back pressure phenomena due to the resistance of oil globules in the sand. The speaker maintained that when oil was removed from sands near wells the condition finally attained

was not of successive gas and oil globules in a tube, but of complete passage ways through which the gas could move, though even when that condition came into play, the gas, as it drove through, still carried a certain amount of oil with it. The efficiency of gas drive depended very materially on the upward or downward movement of the gas in the sand and it was much greater when the gas could be driven down a dip so that the gravity of the oil helped the condition.

The author of the paper had made a very interesting suggestion that producing wells should be placed centrally and surrounded by rings of wells from which a direct gas drive could be obtained. There was, however, the danger that the gas movements would follow the layers of more open strata and leave the other portions poorly drained. We should not lightly give up our present practice of equal spacing until we were sure that this danger could be overcome. The speaker doubted whether gas drive would ever be the equivalent of oil mining. In the latter it was possible to control the local flow of oil in the strata, but in gas drive it was impossible to exercise this local control.

The author had remarked that the percentage of oil extracted was only 25. This indicated great room for improvement. It was, the speaker said, theoretically and experimentally feasible to obtain from sand something like 75 to 80 per cent.; the industry had therefore a long way to go. The author's paper served a very useful purpose in drawing attention to the fact that present methods of production left much to be desired and its publication would focus attention and promote discussion on what was a very important aspect of the industry.

Captain D. Comins said that the subject which Mr. Ellis had so admirably reviewed covered such a tremendous range of controversial points that it was practically impossible to do more than touch on one or two of them. He agreed with Prof. Illing that conditions could not be completely cut and dried. In one field it was quite possible to have, not only more than one of the different types of control—for example, volumetric and capillary control—but also different graduations of any one of the controls; for example, a control that was volumetric in terms of commercial time and hydraulic in terms of geological time. The task of attempting to express field conditions in mathematical symbols was most complicated and difficult.

One of the most important essential points in any consideration of the whole subject was that of how much gas would be in solution in the oil and the speaker had been disappointed to find that this problem was only dealt with superficially in Mr. Herold's book, although dependent problems were treated in great mathematical

detail. Practically none of the literature which the speaker had read, nor any of the experiments that he had seen described, dealt with this point specifically. Papers always mentioned in a casual way that the gas in solution varied with the pressure of the oil, but the pressure itself was never defined. Was it the actual pressure at any point—that was to say the pressure on the gas-oil interface plus the static head of the oil—or was it the pressure at the gas-oil interface ?

It was difficult for States to lay down equitable legislation, on the lines Prof. Lilley had described, whilst this problem remained unsolved. The State could not lay down how much gas was to be produced with oil unless they knew how much gas was in solution with that oil. If the gas was in solution, it must be produced, and if the quantity was regulated, the producers would have to put back the remainder.

The solution of the problem was difficult. It was possible to make experiments : to take a sample of crude oil at high pressure, take off the gas at different pressures and find the quantity of gas in solution, drawing a curve to show the relation between solubility and pressure. In this experiment, however, the pressure was the pressure at the gas-oil interface, as the head of the column of oil in such a surface experiment was negligible in comparison. If an attempt was made to ascertain the variation of the actual gas-oil ratio in actual wells with the pressure at the gas-oil surface or at the bottom of the well, the measured gas-oil ratio is usually found to be somewhat higher than the figure obtained from the curve obtained by surface experiment. It was extremely difficult to arrive at final conclusions, because the producing gas-oil ratios were influenced by other factors such as porosity conditions.

A strong case could be made out for considering that gas in solution varied with the dome pressure—*i.e.*, the pressure at the gas-oil interface—in a virgin field where there was perfect equilibrium ; but that when equilibrium had been disturbed by production, it would take a very long shut down to re-establish gaseous equilibrium in the oil on the flanks of the field where the actual or hydrostatic pressure on the oil was higher than dome pressure. Under such conditions there might be a temporary relation between gas content and actual pressure—*i.e.*, more gas in solution down the flank during the period of gaseous instability. The only way in which it was possible to obtain finality was by taking actual samples from the reservoir at varying pressures and it was very difficult to bring up a sample at full pressure without any loss. This was a point for possible discussion and investigation.

It had been proved, by taking pressures in wells at different depths, that the gravity of the oil was appreciably decreased by

gas in solution ; but if the gas in solution was to vary with the actual pressure, and the argument were carried to its logical limits, the oil at the bottom of the reservoir would be lighter than at the top, because there would be more gas in solution. This would, of course, be inconsistent with equilibrium and supported the case for considering that for equilibrium the gas in solution would be dependent on the dome pressure.

Mr. Ellis had mentioned that, at the ordinary temperatures and pressures that existed in reservoirs, propane and butane existed as liquids owing to the fact that reservoir pressures were higher than their vapour pressures for those temperatures. The speaker did not, he said, consider this to be the case. It seemed possible to have free propane and butane at very high reservoir pressures, entirely dependent on the partial pressure of the propane and butane ; that depending again on the proportion of the propane-butane percentage in the gas and not on the actual reservoir pressure. Therefore, the example quoted, in which it was stated that propane at 100° F., and a pressure of 260 pounds would exist as a liquid if the pressure were more than 260 pounds, was not convincing, though possibly the speaker had, he said, misunderstood Mr. Ellis's intended meaning.

Mr. Ellis had suggested that, with hydraulic control, it would be possible to drill a ring of producers immediately below the gas-oil level and that such wells would go on producing until the end of the field. That suggestion assumed that no gas dome was formed under conditions of hydraulic control, an assumption which the speaker had frequently noted in oil field literature and which he considered to be misleading. It was easy to see that the pressure in the gas dome was due to the head of water less the head of oil above oil-water level. That was the initial dome pressure. Suppose the oil-water level rose after production to 1000 ft. above its original level, the dome pressure was then the head of water, less the sum of the head of the 1000 ft. of water and the head of the oil above the water. The result was that the dome pressure had dropped, because it was necessary to subtract at least the difference between 1000 ft. of water and 1000 ft. of oil. A gas dome must have been formed. Therefore, unless there had been a leakage of gas, due to fracturing of the structure, or production from gas wells, the gas-oil level would drop and the ring of producers drilled just below gas-oil level would go to gas. In principle, of course, the policy of drilling wells high up the flank, under conditions of hydraulic control was not disputed ; but the speaker wished to make the point that such wells should not be drilled too close to gas-oil level.

Dr. A. Wade doubted if a paper of this kind deceived anybody. Treatises like Herold's work on the production of oil gas and water, and papers like the present one were accepted generally as being studies of a purely theoretical nature. For the purely theoretical examination of such problems as those dealt with, in order that any mathematical treatment, based upon the functions of well-known natural laws, can be applied, more or less simple, constant and uniform conditions had to be postulated, but everybody concerned knew that in Nature, in actual work in the field, the conditions are likely to be much more complex. In oilfield practice we have to deal with, and know that we shall have to deal with, all sorts of complications which are not envisaged in a purely theoretical treatment of the problems.

These facts, however, do not destroy the value of papers such as these, in fact they should be regarded as invaluable by practical men. The latter do not always realise that their rule-of-thumb methods are based on some sort of theory and that the success of such methods is only proportional to the soundness of this underlying theory. These theoretical studies are necessary. They must provide the bases for all improvements in method, in efficiency of working and in the means employed for the elimination of waste. Waste in connection with the oil industry is appalling and impresses everybody who examines the working conditions. The present paper deals only with the least noticeable, possibly the least harmful, aspect of waste, the waste which occurs when a field is abandoned with something like three-fourths of its original oil contents still in the sands. This aspect is possibly least harmful since, so long as this oil remains in the sands, there is a possibility that means of recovering it will one day be discovered.

The speaker gave instances of waste on oilfield areas and of the harmful effect on oil production caused by ill-considered waste of gas by drilling unwanted gas wells.

Speaking of Mr. Ellis's suggestion that 18 surrounding wells of small diameter should be drilled around a central well and used as pressure intakes in order to drive a maxima of oil from the sand into a centrally-placed well, he thought the scheme to be impracticable. For success it would require peculiarly ideal conditions. In the field all sorts of difficulties, some of them so obvious that they need not be specified here, were likely to prevent any such scheme being effective. It would probably be found to be cheaper, especially in the shallower fields, to adopt the methods used by French engineers in Alsace and mine the oil-sands by means of shafts and galleries.

He complimented the author on a very useful and suggestive paper.

Mr. L. Owen congratulated Mr. Ellis on a very lucid précis of Herold's theories. Herold's work must be considered as a wonderful piece of pioneering, but it contained, he was afraid, a lot of very difficult reading, and he (Mr. Owen) could not pretend that he followed a large part of Herold's reasoning, nor could he agree with some of the parts which he understood.

One of the views had struck him as badly expressed: that was the cone scheme. In practice the cone was not a cone at all. Oil was lost progressively less as the distance from the well increased, and the area affected would possess a cylindrical shape in homogeneous media. The amount of loss was represented mathematically by a cone, but when interference figures were introduced and the cones were used again—particularly when the question of dead oil was brought in—an entirely wrong idea was obtained of the events taking place underground, at least by the ordinary layman. He would like to see in future the real character of that cone emphasised; that it was purely a mathematical conception that had nothing to do with the actual distribution of oil in the sand.

The speaker then discussed Herold's curve of potential velocity of production, drawing co-ordinate and abscissa to represent time and potential velocity, or "production." Herold, he said, gave three curves, respectively illustrating volumetric, hydraulic and capillary production. The speaker expressed himself in entire agreement with most of the criticisms with reference to capillary production in the foregoing discussion; in fact, he did not think that capillary control could exist exclusively under oilfield conditions. He then drew some actual curves showing various types of extremely irregular production, and asked what kind of control a well was under which gave production curves of this shape. There were, of course, possible geological explanations of all these curves, but unfortunately a mathematician and a geologist working in conjunction could explain away almost any production anomaly. He would be the last person, however, to suggest that Herold's work did not represent a much-needed classic. Dr. Herold had given the industry, for the first time, a peg on which a mathematica analysis of production could be hung. The book was a remarkable one, and he would recommend anyone who had not done so to read it.

Mr. Ellis, in reply to the President, said that, since his paper was an attempt to explain and to show possible methods of increasing production, he would ask to be excused from discussion of the question of over-production and restriction.

In reply to Professor Lilley, he said that it was not necessary to complete the ring of air-wells before production could be started, as the centre well would, if necessary, produce any oil which was

due to it under capillary control before the ring came into operation. The air-wells, could therefore, be drilled at any time, but the earlier, of course, the better, as there would be less vitiated oil to deal with.

He said that it was hardly possible to deal with all Professor Illing's remarks in a few words. He had searched everywhere for some form of control other than the capillary, which would restrict production to a definite area around any one well and finally, for all practical purposes, stop production from that well. The type of resistance required was one which was independent of speed, whereas normal resistances to fluid motion depended on speed. It was known that two wells drilled one at each end of a sand field did not affect one another, and that little, if any, interference was to be noticed in wells spaced comparatively closely together. If the resistance to fluid motion decreased with the speed, the effect of production from any one well would be noticeable over much larger areas than is the case in practice. It was the lack of any other form of resistance known to the speaker that had induced him to enquire into Herold's theories. If Professor Illing could point out a type of resistance having the same properties as those outlined by Herold, he would be pleased to accept it as an alternative to capillary control.

Mr. Ellis agreed that one part of a field could be under capillary control and one under volumetric control, but the same part could not be under capillary and volumetric control, or volumetric and hydraulic control at the same time. He suggested as a simile a train being assisted up an incline by a banking engine. The banking engine behind could not be half pushing the train; it must either be in contact with it and doing some work on it, or not in contact with it and doing no work. It was doing something or nothing. If it were doing something, then the train was partially at least under its control; if it were doing nothing, the train had to proceed under its own power. Similarly, there was no half-way house between hydraulic or volumetric control and capillary control, *i.e.*, the water head or gas pressure were either assisting in production under hydraulic or volumetric control, or production was occurring without their aid under capillary control.

Professor Illing, he said, had stated his disbelief in capillary control as he had found experimentally that gas passages were formed and that gas came through them, leaving the oil behind. This was known to happen to a certain extent, but the speaker did not see that it formed a good argument against capillary control. The gas had to enter these passages, and in getting from the fine capillaries to the passages it must bring oil with it, and the oil would flow down the passages to a large extent, as it would if the passages were perforated cased extensions of the well.

A considerable amount of gas driving had been done in Burma, and it did not seem to make much difference in what direction the drive was set whether along or across the dome. A considerable expenditure of gas was necessary, and it was never certain how much of the oil which was extracted would have been produced by more normal methods in a slightly longer time or what was the actual gain from gas drives; he did not think that as at present practised they were a particularly efficient way of increasing the ultimate production from an oilfield.

The reply to Captain Comins's remarks on the mixture of controls was the same as that which he had given to Professor Illing. On the matter of the solubility of gas in oil, he had been unable to find any authoritative information, and had in fact relied in part at least on figures given him by Captain Comins some time ago. He had done his best to give some idea of the available energy in an oilfield, and though perhaps he had assumed a number of things without complete justification in his model field, he thought it was reasonably certain that gas which was absorbed in the oil was worth a great deal more in a field under any form of control than the gas in the dome above the oil.

In one part of his paper he had recognized that propane and butane existed as gases under the law of partial pressures in the gas above the dome, but he had said elsewhere that they did not give up their energy until the dome pressure fell to a point at which they could gasify in bulk and in this he thought that he was right.

He was glad, he said, to have Dr. Wade's support. He had expected to hear much from opponents of the theory, and it was pleasant to find someone who stood up for it. Any attempts to arrive at the theory of oil production were worth while; if they did not lead to the correct solution, they at least showed a direction in which future investigators should not go. Dr. Wade had suggested that 18 wells round a single well would be expensive, and that it would be cheaper to mine. The 18 were, however, only the same number as would have to be drilled in any case to extract the oil under present methods before mining commenced. With 18 wells round the central well, it might be possible to extract all the oil, whereas with 18 wells at the usual spacing, it was only possible to extract about a third of the available oil.

In regard to Mr. Owen's comments he thought that he had made it clear that the cone was only a mathematical representation. He had been deceived by it once or twice himself, but now had it fairly clearly in his mind, and believed that the treatment of the matter in his paper was true to the mathematical conception.

He admitted that it was impossible to say under what kind of control the wells were whose production curves Mr. Owen had

represented on the blackboard, as no information was given as to the units of volume and time in which they were drawn, or as to their relation, both in time and space, to other wells in the oil reservoir. Even if they were isolated wells from which a regular curve could be expected, there was always the possibility of gas being held up temporarily in one part of the reservoir and then breaking through. The strata were not homogeneous or completely stable, and a study of the actual conditions would no doubt reveal to what extent and why the production from the wells was so erratic. Herold's theory worked on the assumption that the strata of a reservoir were homogeneous, but at the same time it gave an idea of what was to be expected from natural reservoirs. No one asserted that production would follow exactly the theoretical laws, but it was suggested that a knowledge of these laws would assist producers in improving their methods of oil winning. He thought—as Mr. Owen had said—that Herold's book was a valuable contribution to the science of oil production.

On the motion of the President, a hearty vote of thanks was accorded to Mr. Ellis for his interesting paper, and the meeting terminated.

Mr. L. Owen, in a written contribution to the discussion, stated that one of the production curves he had illustrated was founded on observations made on a well in Colombia some years before Herold's work was published. This well was the only producer in the area and interference was, therefore, out of the question.

The other production curves illustrated were based on results from two wells in Venezuela drilled 500 ft. apart into what was, geologically, the same stratum of sand. The lack of sympathy between these curves negatived any suggestion of interference.

Using Herold's analysis, these wells appeared to be sometimes under hydraulic control and sometimes under volumetric and/or capillary control. Often the curve did not, even approximately, correspond with any of the theoretical forms deduced by Herold. He had drawn the "production of oil" curves only, but he had, of course, used the "pressure" curves when attempting any analyses of control. Personally, he had found it extremely difficult in practice to differentiate, satisfactorily, between volumetric and capillary control. At first he had rather favoured capillary control as a solution to the behaviour of certain wells, but critical analysis made him doubtful as to the truth of his original conclusions.

It must be remembered that the data available are obtained from the surface. This is separated from the actual reservoir by a tube (the casing) whose length is usually very great in comparison to its diameter. It is probable, therefore, that the "volume" curve and the "pressure" curve, as measured at the

casing head, may be considerably "out of phase" under such conditions and that the deductions drawn from them are liable to be misleading.

Both Herold and Ellis emphasised that no reservoir could be in more than one control at the same time but, surely, it was conceivable that two or more controls could exist in equilibrium ?

Mr. B. J. Ellis, in reply to Mr. Owen's written contribution, said he was unable to comment more fully on the production curves mentioned as the further particulars given were not specifically related to any one of them. One of the curves appeared to be a daily production curve extending over two or three days, while two others were complete decline curves and seemed to show a change in control from "hydraulic" to either "volumetric" or "capillary." Such a change is to be expected if gas energy is wasted, and it is possible that a fuller appreciation of Herold's theories by those in charge of the field at the time would have resulted in the adoption of more efficient producing methods and the continuance of production under hydraulic control with a consequent greater ultimate recovery of oil. However, so little information is given by Mr. Owen that detailed consideration is quite impossible; it is not even stated whether the wells were flowing or being artificially produced, or whether they were producing throughout their life against a constant or a continually varying back pressure or oil head. Such particulars are required before the practical aspect can be properly appreciated, and they are essential factors in all the theoretical formulæ.

The reply to Mr. Owen's suggestion that two or more controls could exist in equilibrium is, of course, that no form of control exists in equilibrium. The controls only come into operation when equilibrium is upset.

THE INSTITUTION OF PETROLEUM TECHNOLOGISTS, PERSIAN BRANCH.

AT THE THIRD ANNUAL GENERAL MEETING of the Persian Branch of the Institution of Petroleum Technologists, held at the Abadan Gymkhana Club, on April 30th, 1930, the following paper was read :—

The Vapour Pressure Curves of Motor Spirits.

By P. MEYER, B.Sc., A.I.C. (Associate Member).

SUMMARY.

A variety of experimental data from a large number of sources, for the air-free vapour pressure curves of gasoline and motor spirits, has been collected and systematised.

It is found that these curves are all of the same type, and a single curve based on the Ramsay-Young Boiling Point Law fits the data with good accuracy.

Two methods of calculating the true vapour pressure curve from the apparent vapour pressure curve are proposed. In this way the difficult physical operation of separating dissolved air without removing the light hydrocarbon gases, is avoided; and a more accurate result may be obtainable.

The true vapour pressure curves of gasolines and motor spirits are in agreement with a value of Trouton's constant of 17·6. This value is more apparent than real, the actual latent heat of vaporisation corresponding to the normal value of Trouton's constant of 20·21.

THE full knowledge of the vapour pressure characteristics of an oil involves knowledge of the following three factors :—

1. True vapour pressure under given conditions of temperature and liquid/vapour volume ratio; and rate of increase of the true vapour pressure with temperature.

2. Dissolved air pressure under given conditions, and the rate of increase of dissolved air pressure with temperature.

3. Variation of vapour pressure with amount vaporised.

Numerous methods of plotting vapour pressure curves have been advanced from time to time. The most useful and systematic of these employ the Ramsay-Young Boiling Point Law.

Ormandy and Craven[1] observed that by this method a standard vapour pressure curve might be constructed which would fit most pure hydrocarbons.

Brown[2] shows a vapour pressure chart for pure hydrocarbons constructed by this method.

Ashworth[3] derived from the Clausius-Clapeyron equation an equation applicable to most pure hydrocarbons at pressures below 760 mm.

The Ramsay-Young Boiling Point Law may be deduced as follows:—

In the integrated form of the Clausius-Clapeyron equation,

$$\text{Log}\,\frac{P_1}{P_2} = \frac{JL}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

where P_1 = vapour pressure at a temperature T_1 (absolute).

P_2 = " " " " T_2 "

J = mechanical equivalent of heat.

L = molal latent heat of vaporisation.

R = gas constant.

Now denoting T_2 by t = boiling point at 760 mm., and P_2 by p = 760 mm., we have

$$\text{Log}\,\frac{P}{760} = \frac{JL}{R}\left[\frac{1}{t} - \frac{1}{T}\right]$$

where P is the vapour pressure at any other temperature T.

By Trouton's Law, L = Ct where C is Trouton's constant.

$$\text{Log}\,\frac{P}{760} = \frac{JC}{R}\left[1 - \frac{t}{T}\right]$$

or more simply, since J, C, and R are constants,

$$\text{Log}\,P = K_1 - K_2\,\frac{t}{T} \quad \ldots\ldots (1)$$

which expresses algebraically the Ramsay-Young Boiling-Point Law. The equation represents a straight line, but the graphs obtained experimentally show a slight curvature.

A large amount of vapour pressure data for pure hydrocarbons is plotted on Graph No. 1.

It may be noted firstly that the data may be represented with fair accuracy by three curves.

Curve ACE for methane and ethane.

BCE for propane and butane.

BCD for pentane-dodecane.

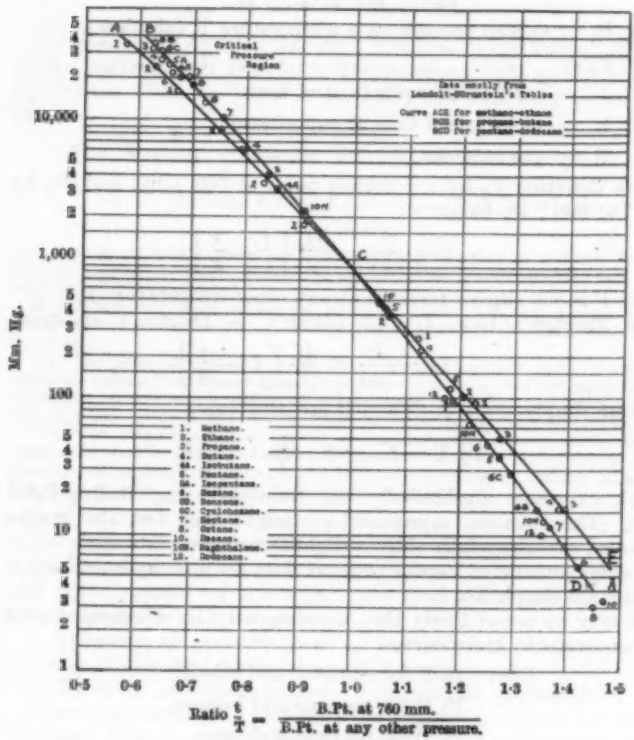
These curves overlap so that only two curves are shown on Graph 1.

It may be noted secondly that the slope of the vapour pressure curve, plotted in this manner, tends to increase with increasing boiling point. The slope is mathematically proportional to Trouton's constant; and the deviation observed is probably due to the fact that Trouton's constant tends to increase with increasing boiling point.[4]

Algebraically the equations to the curves in Graph 1 are :—

Methane-ethane (ACE).

$$\text{Log}_{10}\,P = 6{\cdot}75 - 3{\cdot}59\left(\frac{t}{T}\right) - 0{\cdot}28\left(\frac{t}{T}\right)^2 \quad \ldots\ldots(2)$$



GRAPH 1.

VAPOUR PRESSURES OF PURE HYDROCARBONS.

Propane-butane (BCE).

$$\text{Log}_{10}\,P = 7{\cdot}33 - 4{\cdot}45\left(\frac{t}{T}\right) \quad \ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Pentane-dodecane (BCD)

$$\text{Log}_{10}\,P = 6{\cdot}78 - 3{\cdot}10\left(\frac{t}{T}\right) - 0{\cdot}80\left(\frac{t}{T}\right)^2 \quad \ldots\ldots(4)$$

Differentiating equation 4 we have

$$\frac{dP}{dT} = \frac{P}{T^2}\left[7{\cdot}14\ tT + 3{\cdot}69\ t^2\right]$$

and in the neighbourhood of the boiling point, where

$$t = T \text{ approx.}, \quad dT = 0{\cdot}00012\ T{\cdot}dP$$

which is the expression given by Young for the correction of boiling points for small changes of atmospheric pressure.

Substituting in the Clausius-Clapeyron equation the value of dP/dT given above, we have

$$L = \frac{R}{JT}\left[7{\cdot}14\ Tt + 3{\cdot}69\ t^2\right]$$

$$= 1{\cdot}97\left[7{\cdot}14\ t + 3{\cdot}69\ \frac{t^2}{T}\right]$$

$$= 14{\cdot}06\ t + 7{\cdot}27\ \frac{t^2}{T}$$

This gives a value for the latent heat of vaporisation at any temperature, as calculated from the vapour pressure curve; and at the boiling point, $L = 21{\cdot}33\ t$; giving a theoretical value for Trouton's constant of 21·33, as compared with an actual value of about 20·7.

It is of interest to see to what extent the vapour pressure curve of a mixture of hydrocarbons may be predicted, by applying Raoult's Law.

Raoult's Law states that $p = nP$

where p = vapour of liquid at molal concentration n.

P = vapour pressure of the pure liquid at the same temperature.

Then at a temperature T_1, $p_1 = nP_1$

T_2, $p_2 = nP_2$

Substituting for P_1 and P_2 in the Clausius-Clapeyron equation, we have :—

$$\text{Log}\frac{p_1}{p_2} = \text{Log}\frac{nP_1}{nP_2} = \text{Log}\frac{P_1}{P_2}$$

$$= \frac{JL}{R}\left[\frac{1}{T_2} - \frac{1}{T_1}\right]$$

Assuming that Trouton's Law is still valid, equation 1 may be deduced exactly as before, and the curve for pure hydrocarbons is valid for mixtures obeying Raoult's Law.

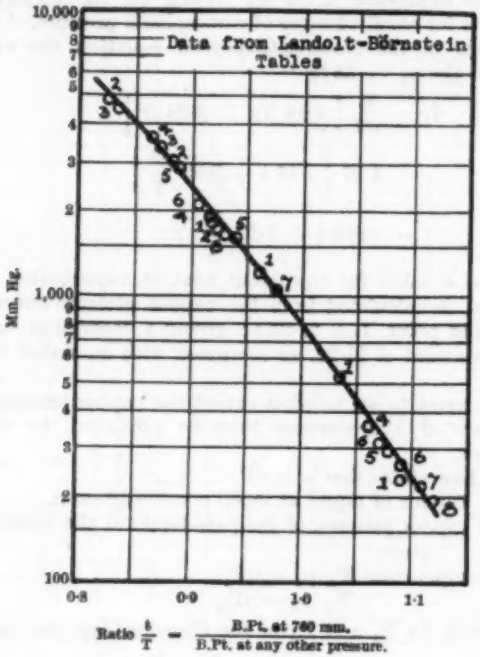
It may now be observed that the same reasoning holds good for mixtures not obeying Raoult's Law, provided the deviation is the same at all temperatures.

For let r be the deviation, such that :—

$$p_1 = rnP_1$$
$$p_2 = rnP_2.$$

Then equation 1 may be deduced exactly as before.

No published observations on the vapour pressure curves of specific hydrocarbon mixtures appear available. Some results for



GRAPH 2.

VAPOUR PRESSURE CURVES OF CHLOROFORM-ETHYL ETHER, ACETONE, CHLOROFORM-ETHYL ETHER AND CHLOROFORM-ACETONE MIXTURES.

1 = 100	mol.	%	$CHCl_3$ +	0	mol.	%	$(C_2H_5)_2O$
2 = 0	,,	,,	,,	100	,,	,,	,,
3 = 10	,,	,,	,,	90	,,	,,	,,
4 = 50	,,	,,	,,	50	,,	,,	,,
5 = 70	,,	,,	,,	30	,,	,,	,,
6 = 0	,,	,,	,,	100	,,	,,	$(CH_3)_2CO$
7 = 30	,,	,,	,,	70	,,	,,	,,
8 = 80	,,	,,	,,	40	,,	,,	,,

chloroform—acetone and chloroform—ether mixtures are, however, given in the Landolt-Bornstein tables, and have been plotted in Graph 2. Although these mixtures deviate widely from Raoult's

Law, the curve obtained is practically coincident with the curve for the pure components. It is also of interest to note that sharply fractioned petroleum cuts of narrow boiling range—10° C. to 20° C. —are found to correspond closely with the pure hydrocarbon series.

The boiling range of such mixtures is, however, very much narrower than in the case of motor spirits. Brown [2] concluded that the vapour pressure curve of a hydrocarbon mixture was of a different type from that of the pure components.

Some doubts may therefore be expressed with regard to the reliability of theoretical predictions of the vapour pressure curves of complex mixtures.

As in the case of pure hydrocarbons, experimental results of the vapour pressure curves are the only satisfactory guide.

It is found that the results for complex mixtures may also be systematically represented by the Ramsay-Young Boiling-Point Law.

Before proceeding to discuss the results, however, it is convenient to review the experimental methods which have been employed.

In plotting vapour pressure curves of mixtures, the term " boiling point " is used to denote the temperature in the oil when the vapour pressure is 760 mm.

Normally the sample contains non-hydrocarbon gases, such as air, in solution in the spirit. Ideally these could be removed by low temperature or high pressure fractionation, and the true vapour pressure would be directly determinable in, *e.g.*, an Andrews' apparatus at zero free space or vapour volume.[5] Traces of water are removable by a suitable desiccating agent.

A number of more or less approximate methods have been used for the removal of dissolved air or for the elimination of dissolved air pressure, as follows :—

(*a*) *Rhodes and McConnell's Method*[6].

The sample of oil is agitated in vacuum, partial vaporisation occurring ; the liberated gas is restored to about atmospheric pressure and the non-condensed portion is removed. The operation is repeated until no further non-condensible gas separates from the oil.

(*b*) *Bridgeman, Aldrich and White's Method.*[7]

The sample is cooled with liquid air and dissolved gas is removed by the application of vacuum.

(*c*) *Tizard and Marshall's Method.*[8]

The vapour pressure is determined at various vapour/liquid ratios ; the extrapolated curve gives the gas free vapour pressure.

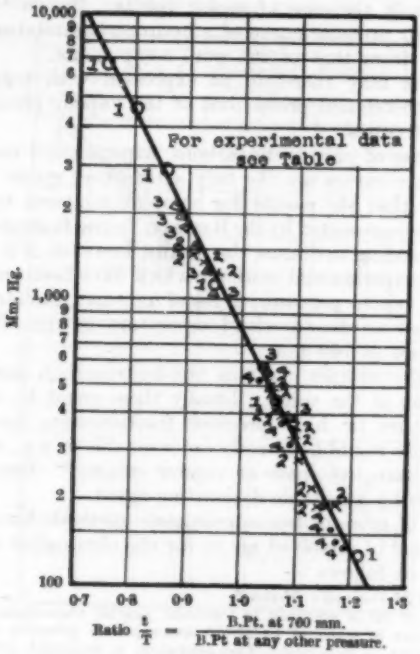
(*d*) *Refluxing Method.*

A large volume of sample is boiled under a small reflux condenser to expel dissolved gas. The vapour pressure curve is then determined in an Andrews' apparatus at zero free space.[5]

(*e*) *Beistle-Prather Bomb Method.*[3]

Two vapour pressure curves are determined ; the free space in one case being twice that in the other case. Assuming that the air pressure with the smaller vapour space is twice that with the larger vapour space, the true hydrocarbon vapour pressure may be calculated.

Now in regard to the absolute determination of vapour pressure at a given temperature, none of these methods are entirely free from objection. We are at the moment concerned, however, with the shape of the vapour pressure curve—*i.e.*, the rate of increase of vapour pressure with temperature.



GRAPH 3.

EXPERIMENTAL VAPOUR PRESSURES OF AIR-FREE MOTOR SPIRITS.

Determinations by :—
Andrew's Apparatus 1
Rhodes and McConnell 2
Beistle-Prather 3
Tizard and Marshall 4
Straight line is for Bridgeman, Aldrich and White.

A large amount of vapour pressure temperature data by all the above methods has been collected. The data, given in the Table at the end of this paper, is shown graphically in Graph No. 3.

Graph 3 also includes data by Andrews' apparatus for a compression gasoline prepared from an air-free gas, and subsequently vented from 45 lb. gauge to atmospheric pressure. This product

was therefore free from dissolved air and no preliminary de-aeration of the sample was effected. The sample was an unfractionated product.

It is interesting to note that results by all these diverse methods may be represented with fair accuracy by a single curve, the equation to which is that proposed by Bridgeman, Aldrich and White,[9] viz. :—

$$\text{Log}_{10}P = 6{\cdot}76 - 3{\cdot}88\left(\frac{t}{T}\right) \quad .. \quad .. \quad (5)$$

This curve may therefore be accepted as satisfactorily representative of the vapour pressure curves of gasoline and motor spirits.

Comparing this curve with the pure hydrocarbon curves on Graph No. 1, curve BCE for propane-butane or curve BCD for pentane-dodecane, it will be noted that the rate of increase of pressure with temperature is less than in the case of pure hydrocarbons.

The general effect of dilution on lowering the slope of the vapour pressure curve may be predicted as follows :—

For a pure hydrocarbon :

$$\text{Log}_{10}P = a - b\frac{t}{T}$$

Hence
$$\frac{d\,(\text{Log}_{10}\,P)}{d\left(\frac{t}{T}\right)} = -b \quad .. \quad .. \quad (6)$$

Now if the hydrocarbon is diluted to molecular concentration n in a non-volatile solvent, giving a vapour pressure p such that $p = nP$:

Then
$$\text{Log}_{10}\frac{p}{n} = a - b\frac{t}{T}$$

or
$$\text{Log}_{10}p = \text{Log}_{10}n + a - b\frac{t}{T} \quad .. \quad .. \quad (7)$$

The new boiling point, t^1, at 760 mm. at this dilution may be found by substitution :—

$$\text{Log}_{10}\,760 = 2{\cdot}88$$
$$= \text{Log}_{10}n + a - b\,\frac{t}{t^1}$$

Hence $bt = t^1\,(2{\cdot}88 - \text{Log}_{10}n - a)$
$= t^1\,(-b - \text{Log}_{10}n)$ (since $a - b = 2{\cdot}88$)

Substituting for bt in equation (7) we have :

$$\text{Log}_{10}p = \text{Log}_{10}n + a - (b + \text{Log}_{10}n)\,\frac{t^1}{T}$$

Hence for the diluted mixture :

$$\frac{d\,(\text{Log}_{10}p)}{d\left(\frac{t^1}{T}\right)} = -\,(b + \text{Log}_{10}n) \quad .. \quad .. \quad (8)$$

Thus the slope of the original curve, plotted by the Ramsay-Young Boiling Point Law, is —b (equation 6); while the corresponding slope for the diluted mixture is $-(b + \mathrm{Log}_{10}n)$ (equation 8). Since n is less than unity, $\mathrm{Log}_{10}n$ has a negative value, so that $b + \mathrm{Log}_{10}n$ is numerically less than b.

Beyond demonstrating the qualitative fact that the slope of the vapour pressure curve may be less steep for a diluted mixture than for a pure component, it is doubtful if further deductions would be valid. Equation 5 could not, in all probability, be deduced theoretically, and it would be difficult to assess the deviations from Raoult's Law which would occur. Experimentally equation 5 fits the facts satisfactorily, however, as is shown by Graph No. 3.

Having now developed a vapour pressure/temperature curve representative of many types of apparatus and gasoline, we may investigate the other two factors associated with complete knowledge of the vapour pressure of a mixture; namely, the behaviour of dissolved air, and the variation of vapour pressure with amount vaporised.

Experimentally the complete removal of dissolved air from a volatile spirit, without loss of any hydrocarbon, is a matter of difficulty. With incomplete removal, the small quantity remaining may upset results, particularly if the vapour pressure is determined at zero space; while in effecting complete removal of dissolved air, gaseous hydrocarbons, such as propane and butane, may also be partially removed.

It is apparant therefore that a method whereby the true hydrocarbon vapour pressure might be calculated from the observed total vapour pressure, thus avoiding the experimental separation of dissolved air, would be of use.

In the following pages an analysis of apparent vapour pressure curves is made. The apparent vapour pressure curve was determined by Rhodes and McConnell's apparatus[6] without expulsion of any dissolved air or gas, at 2 : 1, 4 : 1, and 8 : 1 liquid/vapour volume ratios.

Two methods of calculation have been developed :—

Method 1.—The apparent vapour pressure curve is regarded as the sum of two component curves, viz., the true hydro-carbon vapour pressure curve, plus an air pressure curve.

Method 2.—The true vapour pressure at any temperature is calculated from the apparent molal heat of vaporisation.

Method 2 also gives an independent check upon the rate of increase of true vapour pressure with temperature, which is found to be within 5 per cent. of that predicted by equation 5.

A consistent result for the true vapour pressure is found by both methods.

The observed vapour pressure data is referred to as at a 2 : 1, 4 : 1 or 8 : 1 liquid/vapour ratio. The value of the ratio is however unimportant; it suffices that we have 3 vapour pressure curves for the same spirit at any three different ratios; and in no case does the value of the ratio enter into the calculations.

In the experimental determination of the apparent vapour pressure, no exposure of the sample to air was incurred, so that no change in composition of the sample occurred. Actually in the following calculations it would not matter if the sample charged to the apparatus at a 2 : 1 ratio, for instance, contained a different concentration of air from that charged at a 4 : 1 or 8 : 1 ratio. The variation in true vapour pressure with amount vaporised is dealt with later.

Method 1.—In the first place, the behaviour of dissolved air may be dealt with. Air and gas oil of negligible vapour pressure over the temperature range investigated were heated together in a 4 : 1 oil/vapour ratio in Rhodes and McConnell's[6] apparatus.

Temperature °F.	60°	90°	120°	160°
(1) Pressure. Mm. Hg.	723	780	835	907
$\frac{\text{Pressure.}}{\text{Ratio, Pressure at 60°F.}}$	1·000	1·079	1·155	1·255
(2) Pressure Mm. Hg.	450	483	517	565
$\frac{\text{Pressure.}}{\text{Ratio, Pressure at 60°F.}}$	1·000	1·073	1·150	1·255

Now if no oil at all were present, the pressure ratios, calculated on the simple gas laws, would have been 1·000, 1·058, 1·115 and 1·192 respectively. The fact that 30 per cent. of the volume was occupied with oil does not seem to have interfered greatly with the simple gas law prediction.

For the pressure increase in such a case, the following simple relationship may be deduced:—

$$\frac{P_2}{P_1} = \frac{T_2}{T_1} \cdot \frac{1 + rS_1}{1 + rS_2 + Lr\,(T_2 - T_1)\,(S_2 - 1)} \quad \ldots\ldots\ldots (9)$$

where T_2 and T_1 are any two temperatures (absolute),
P_2 and P_1 the corresponding pressure,
S_2 and S_1 the corresponding air solubilities (Ostwald absorption co-efficient),
and r = Vol. oil/vol. vapour at temperature T_1.
L = Co-efficient of cubical expansion of the oil.

While no comprehensive data in regard to the solubility of air in various petroleum products at various temperatures is available, it is known that the solubility does not change much with temperature.[10] Over a narrow temperature range therefore we may

assume that $S_1 - S_2$; and that with a reasonable vapour volume the effect of expansion of the oil will be small; so that equation 9 approximates to:—

$$\frac{P_2}{P_1} = \frac{T_2}{T_1} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots (10)$$

The following data for sample of light benzine was determined in an Andrews' apparatus at zero vapour volume. The pressures recorded are averages between the pressure when a very small bubble of vapour is present, and the pressure just necessary to cause this bubble to disappear.

Temperature.	Original Spirit.	Spirit after boiling in a reflux apparatus to expel dissolved air.	Air Pressure by difference.
	mm.	mm.	mm.
20° C. ..	890 ..	210 ..	680
30° C. ..	990 ..	300 ..	690
40° C. ..	1110 ..	410 ..	700
50° C. ..	1240 ..	520 ..	720

$$\text{Ratio } \frac{\text{Air pressure at } 50° \text{ C.}}{\text{Air pressure at } 20° \text{ C.}} = \frac{720}{680} = 1{\cdot}06$$

The theoretical ratio of the dissolved air pressures in such a case is

$$\frac{P_2}{P_1} = \frac{T_2 S_1}{T_1 S_2}$$

which, if the solubility be assumed constant, again simplifies to equation 10.

$$\frac{P_2}{P_1} = \frac{T_2}{T_1} = \frac{273 + 50}{273 + 20} = 1{\cdot}10$$

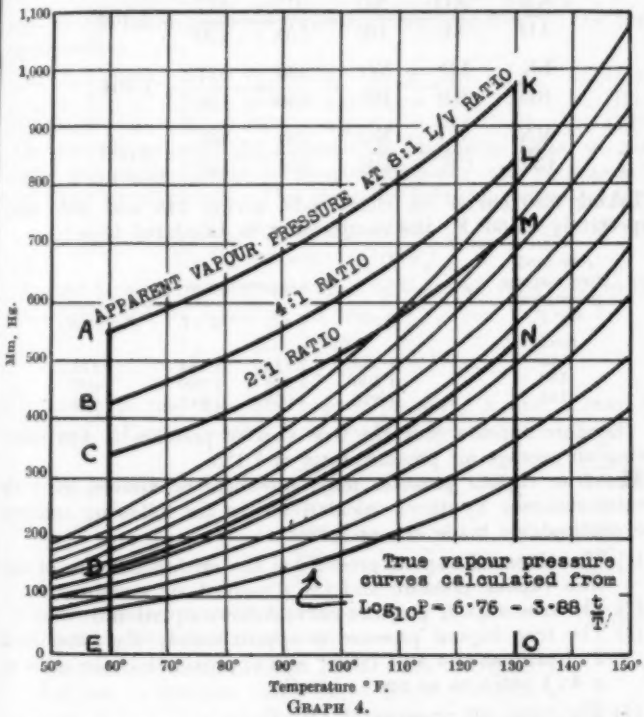
The experimental data is approximate only; and the method of removing dissolved air is open to criticism since a trace of the very volatile components may be removed with the air. Comparing the observed figure of 1·06 with the approximate theoretical figure of 1·10, it is inferred that the pressure due to dissolved gas increases only slowly with temperature, and does not, over the temperature range investigated, deviate widely from the simple gas laws, the pressure at 50° C. being within 4 per cent. of that assuming the simple gas laws.

We have now equation 5, giving the rate of increase of true vapour pressure with temperature; and equation 9, which in certain circumstances simplifies to equation 10, for the rate of increase of air pressure.

The following is the apparent vapour pressure data for a sample of motor spirit, determined by Rhodes and McConnell's[6] apparatus, but without de-aerating—*i.e.*, without expulsion of dissolved gas.

Liquid/Vapour Ratio.	Apparent Vapour Pressure, Mm. Hg.	
	At 60° F.	At 130° F.
2 : 1	338	730
4 : 1	430	836
8 : 1	553	973

Assuming that the observed pressure is the arithmetic sum of true hydrocarbon vapour pressure, following equation 5, and



GRAPH 4.

GRAPHICAL DERIVATION OF TRUE VAPOUR PRESSURE FROM APPARENT VAPOUR PRESSURE.

dissolved air pressure, following equation 10, an approximate graphical analysis of this data may be made by a trial and error method. In Graph 4 a series of true vapour pressure curves have

been plotted, all corresponding with equation 5. The apparent vapour pressure curves, AK, BL, CM, are drawn in heavy lines. By trial a true vapour pressure curve is selected which gives an air pressure increase in accordance with equation 10. Taking the readings at 60° F. and 130° F., we have :

$$\frac{T_2}{T^1} = \frac{460 + 130}{460 + 60} = 1{\cdot}135$$

Taking for trial the curve DN, giving 150 mm. at 60° F., the ratio of the air pressures at 130° F. and at 60° F. is found to be :—

$$\frac{KN}{AD} = \frac{KO - NO}{AE - DE} = \frac{973 - 527}{553 - 150} = 1{\cdot}106$$

$$\frac{LN}{BD} = \frac{LO - NO}{BE - DE} = \frac{836 - 527}{430 - 150} = 1{\cdot}104$$

$$\frac{MN}{CD} = \frac{MO - NO}{CE - DE} = \frac{730 - 527}{338 - 150} = 1{\cdot}080$$

Taking also curves on either side, giving 145 and 155 mm. respectively at 60° F., the results may be tabulated thus :—

Assumed true vapour pressure at 60° F.		Air pressure ratios.			
		8 : 1	4 : 1	2 : 1	Average.
mms.					
145	..	1·135	1·114	1·144	1·141
150	..	1·106	1·104	1·080	1·097
155	..	1·075	1·058	1·012	1·048

It therefore appears that the true vapour pressure is 146 mm., giving an average air pressure ratio of 1·135.

The true vapour pressure may, however, be arrived at with greater accuracy by direct calculation. In the following analysis the assumptions made are as follow :—

(1) The observed vapour pressure is the arithmetic sum of the true vapour pressure and the dissolved air pressure.
(2) The true vapour pressure curve follows equation 5.
(3) The true vapour pressure is approximately the same at a 2 : 1 ratio as at a 4 : 1 ratio ; and approximately the same at a 4 : 1 ratio as at an 8 : 1 ratio.
(4) The ratio $\frac{\text{air pressure at } 130° \text{ F.}}{\text{air pressure at } 60° \text{ F.}}$ is unknown, but is approximately the same at a 2 : 1 ratio as at a 4 : 1 ratio, and approximately the same at 4 : 1 ratio as at an 8 : 1 ratio.

For a given liquid/vapour ratio, let

x = true vapour pressure at 60° F.
X = " " " " 130° F.
C = ratio $\frac{\text{Air pressure at } 130° \text{ F.}}{\text{Air pressure at } 60° \text{ F.}}$

Then for the air pressure at 130° F. we have the three following expressions :—

At 2 : 1 ratio, air pressure $= (338 - x_1)\ C_1$,
" 4 : 1 " " " $= (430 - x_2)\ C_2$,
" 8 : 1 " " " $= (553 - x_3)\ C_3$,

and for the total observed vapour pressure at 130° F. the three equations :—

At 2 : 1 ratio, $X_1 + (338 - x_1)\ C_1 = 730$ .. .. (11)
" 4 : 1 " $X_2 + (430 - x_2)\ C_2 = 836$ .. .. (12)
" 8 : 1 " $X_3 + (553 - x_3)\ C_3 = 973$ .. .. (13).

In accordance with the assumptions originally made, we may regard equations 11 and 12 as simultaneous ; also equations 12 and 13 as simultaneous. This gives the following values for C :—

$C_1\ C_2$ average $= 1{\cdot}152$
$C_2\ C_3$ average $= 1{\cdot}114$
} mean 1·133.

It may be noted that these values of C are all very close to the value predicted by equation 10, viz. :—

$$\frac{T_2}{T_1} = \frac{460 + 130}{460 + 60} = 1{\cdot}135.$$

In order to find the true vapour pressure, X and x may be correlated. From equation 5 or Graph 4 we have :—

If vapour pressure at 60° F.	$=$	$\frac{x}{50}$ mm.	then at	130° F.	$=$	$\frac{X}{200}$ mm.
" " "	$=$	100 "	"	"	$=$	370 "
" " "	$=$	150 "	"	"	$=$	527 "
" " "	$=$	200 "	"	"	$=$	675 "
" " "	$=$	250 "	"	"	$=$	830 "

The correlation may be expressed to a 1 per cent. accuracy by the following empirical relationships :—

50 mm. — 150 mm. range $X = 4{\cdot}26x - 0{\cdot}0053\ x^2$
150 mm. — 250 mm. range $X = 3{\cdot}80x - 0{\cdot}0020\ x^2$.

Substituting in equations 11, 12, 13, the expression for X and the approximate values for C_1, C_2 and C_3 indicated above, we have :

$4{\cdot}26\ x_1 - 0{\cdot}0053\ x_1^2 + 1{\cdot}152\ (338 - x_1) = 730$
$4{\cdot}26\ x_2 - 0{\cdot}0053\ x_2^2 + 1{\cdot}133\ (430 - x_2) = 836$
$4{\cdot}26\ x_3 - 0{\cdot}0053\ x_3^2 + 1{\cdot}114\ (553 - x_3) = 973$.

Solving each equation independently for x :—

x_1 = true vapour pressure at 2 : 1 ratio at 60° F. = 147 mm.
x_2 = " " " " 4 : 1 " " " = 143 mm.
x_3 = " " " " 8 : 1 " " " = 152 mm.

From the true vapour pressure at 60° F. the complete vapour pressure curve may be reconstructed by applying equation 5, or by reference to Graph 4.

The following is some more experimental data for a sample of aviation spirit, determined in Rhodes' and McConnell's[6] apparatus without expulsion of dissolved gas.

Liquid Vapour Ratio.	Apparent Vapour Pressure, Mm. Hg. At 60° F.	At 130° F.
2 : 1 ..	340 ..	856
4 : 1 ..	480 ..	998
8 : 1 ..	588 ..	1123

The values for C, calculated as shown in the case of motor spirit, are found to be :—

$$\left.\begin{matrix} C_1\ C_2 \text{ average } 1{\cdot}084 \\ C_2\ C_3 \text{ average } 1{\cdot}157 \end{matrix}\right\} \text{ mean } 1{\cdot}121,$$

from which, using the X equation for the 150 — 250 mm. range, the true vapour pressure is found to be :—

At 2 : 1 ratio 206 mm. at 60° F.
4 : 1 " 204 " "
8 : 1 " 205 " "

Now in calculating these results, the air-pressure/temperature relationship has been regarded as unknown, and is deduced from experimental observations. It is satisfactory, therefore, to find the relationship so near to the theoretically predicted figure. By way of comparison the vapour pressures have been calculated using the theoretical air-pressure/temperature relationship in equation 10; *i.e.*, taking C = 1·135.

	True vapour pressure at 60° F., mm. Hg.			
	Motor spirit sample.		Aviation spirit sample.	
Value of C taken.	Deduced.	C=1·135 (assuming simple gas laws).	Deduced.	C=1·135 (assuming simple gas laws).
At 2 : 1 ratio ..	147	148	206	204
At 4 : 1 ratio ..	148	149	204	200
At 8 : 1 ratio ..	152	147	205	202

It may be noted that over the temperature range and liquid/vapour ratios investigated, no serious error results in regarding the air pressure as obeying the simple gas laws; and the assumptions made at the outset of the calculation appear justified.

Method 2.—In this method the latent heat of vaporisation is investigated. It is known that experimental values of the latent heat may differ from those calculated from the vapour pressure curve. In this analysis, however, the ratio of calculated latent heat terms is employed, so that any error from this source tends to cancel out.

Equation 5 is in agreement with a molal latent heat of vaporisation of 17·6t (t being the boiling point absolute).

$L = (1{\cdot}97)\ (2{\cdot}303)\ (3{\cdot}88)\ t.$

$= 17{\cdot}6\ t.$

The assumptions made are :—

(1) The molal heat of vaporisation of the hydrocarbon fraction is constant, and is equal to 17·6 t.
(2) The vapour pressure is approximately the same at 2 : 1, 4 : 1 and 8 : 1 liquid/vapour ratios.
(3) The non-hydrocarbon pressure may be expressed by an equation similar to the Clausius-Clapeyron equation; the molal heat term L being replaced by a constant B.
(4) The value of the constant B is unknown, but is the same at all the vapour volume and temperature ranges investigated. The constant B is essentially an algebraic constant and may or may not have a physical significance.

Now if P = observed vapour pressure under given conditions.
and x = true " " " "
then the molal hydrocarbon concentration is

$$\frac{x}{P}$$

and the molal non-hydrocarbon concentration is

$$\frac{P-x}{P.}$$

Hence if L is the molal heat of vaporisation of the hydrocarbon fraction, and B the corresponding term for the non-hydrocarbon, we have :—

$$\frac{x}{P}L + \frac{P-x}{P}B = \text{Observed latent heat.}$$

Re-arranging $= A$ say.

$$x = P\frac{A-B}{L-B} \quad .. \quad .. \quad .. \quad .. \quad (14)$$

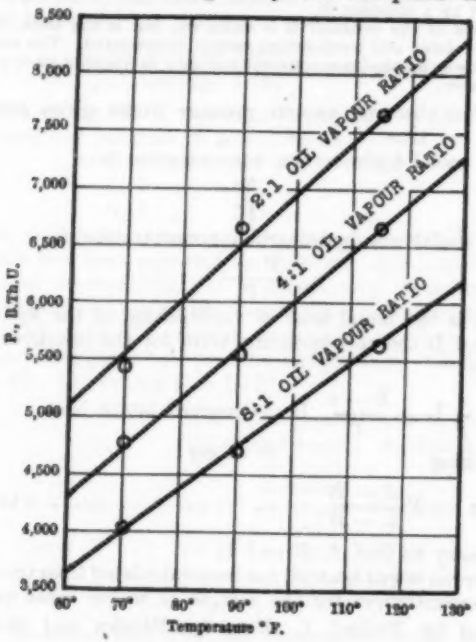
It is necessary to find A, B and L.

The observed latent heat, A, has been calculated from the apparent vapour pressure curve for the sample of motor spirit previously investigated by Method 1. Data by Rhodes and McConnell's apparatus.

$$A = (1{\cdot}97)\ (2{\cdot}303)\ \frac{T_1 - T_2}{T_2 - T_1}\ \text{Log}\ \frac{P_2}{P_1}$$

	Temp.	Observed vapour pressure. mm.	Log vapour pressure.	Differences.	$\frac{T_1\ T_2}{T_2\ T_1}$	A.	Average temperature.
2 : 1 ratio ..	60° F.	338	2·52892				
				> 0·08492	14,040	5420	70° F.
	80°	411	2·61384				
				> 0·09712	15,120	6650	90°
	100°	514	2·71096				
				> 0·15236	11,010	7620	115°
	130°	730	2·86332				
4 : 1 ratio ..	60°	430	2·63347				
				> 0·07495	14,040	4780	70°
	80°	511	2·70842				
				> 0·08116	15,120	5560	90°
	100°	616	2·78958				
				> 0·13263	11,010	6630	115°
	130°	836	2·92221				
8 : 1 ratio ..	60°	553	2·74273				
				> 0·06345	14,040	4045	70°
	80°	640	2·80618				
				> 0·06888	15,120	4720	90°
	100°	750	2·87506				
				> 0·11305	11,010	5650	115°
	130°	973	2·98811				

The value of A found is plotted on Graph No. 5 against the mean temperature. With possibly the exception of the 2 : 1



GRAPH 5.

APPARENT MOLAL HEAT OF VAPORISATION CALCULATED FROM OBSERVED VAPOUR PRESSURE CURVE—MOTOR SPIRIT.

ratio, a reasonable graph is obtained, from which the value of A at any other temperature may be obtained.

B may be found in the following way :—

Let equation 11 be applied to a specified temperature, say, 60° F. Then we have three simultaneous equations for x, at 2 : 1, 4 : 1 and 8 : 1 ratios respectively. Substituting the observed values of P, and the values of A obtained from Graph 5, we have :—

$$x = 338\,\frac{5110 - B}{L - B}$$

$$= 430\,\frac{4350 - B}{L - B}$$

$$= 553\,\frac{3670 - B}{L - B.}$$

Hence 338 (5110–B) = 430 (4350–B) = 553 (3670–B) giving two values of B of 1380 and 1570.

Calculating similarly two values for B at 80° F. at 100° F., and at 130° F., we obtain in all eight values for B :—

B = 1380, 1570,
1360, 1630,
1080, 1320,
170, (o).

Average B = 1060.

B is determined as the difference between two relatively large quantities, and only the average value of B is of significance.

In order to find L, we may assume provisionally that the boiling point—*i.e.*, the temperature at which the true vapour pressure is 760 mm.—lies between 150° F. and 160° F.; so that L will lie between

17·6 (460 + 150) = 10,700
17·6 (460 + 160) = 10,900
Say L = 10,800.

Substituting in equation 14, the true vapour pressure at any temperature may be found directly :—

At 60° F.		At 130° F.	
$x = 338\,\frac{5110-1060}{10800-1060}$	= 140mm. ..	$x = 730\,\frac{3300-1060}{10800-1060}$	= 543mm.
$= 430\,\frac{4350-1060}{10800-1060}$	= 147mm. ..	$= 836\,\frac{7250-1060}{10800-1060}$	= 531mm.
$= 553\,\frac{3670-1060}{10800-1060}$	= 151mm. ..	$= 973\,\frac{6250-1060}{10800-1060}$	= 519mm.
Average true v.p. at 60° F.	= 146mm. ..	Average true v.p. at 130° F.	= 531mm.

These figures may be compared with the average value calculated by the first method, of 149 mm. and 525 mm. respectively. The agreement is as good as can be expected. The boiling-point by equation 5 would be 614° F. absolute, so that the provisional assumption of 150° — 160° F., is in order.

The true hydrocarbon vapour pressure of the sample of aviation spirit previously investigated by method 1, has been calculated in a similar manner.

The average value for B was 900, and the true vapour pressure was found to be as follows :—

	At 60° F.	At 130° F.
Method 1	205 mm.	695 mm.
Method 2	207 mm.	717 mm.

It appears that, over the temperature range investigated, B, which represents L in the Clausius-Clapeyron equation,

$$\frac{dP}{P} = \frac{JL}{R}\frac{dT}{T^2}$$

as applied to the non-hydrocarbon vapour pressure, is an algebraic constant, having a value of 1000 approx. If, however, we are dealing with a pressure increasing in accordance with the simple gas laws, we have

$$\frac{dP}{P} = \frac{dT}{T^2}$$

Hence

$$B = L$$
$$= \frac{R}{J} T$$
$$= 1{\cdot}97\ T.$$

Now T has an average value of 555° F. abs., giving

$$B = 1100 \text{ approx. as against } 1000 \text{ observed.}$$

It thus appears that the dissolved air pressure increases according to the simple gas laws. B is not therefore constant. The error involved however is small.

Graph 5 is very useful in affording an independent check on the true hydrocarbon vapour pressure curve. Assuming L and B to be constant, it follows from equation 11 that at the same apparent molal heat of vaporisation, the same mol. fraction of hydrocarbon is present. The motor spirit at 60° F. and a 2 : 1 ratio, has the same apparent molal heat of vaporisation, 5110, as at 100° F. and an 8 : 1 ratio.

Thus if at 60° F. and a 2 : 1 ratio,

X_1 = true vapour pressure.

P_1 = apparent (total) vapour pressure, so that mol. fraction hydrocarbon $= \frac{X_1}{P_1}$

and if at 100° F. and an 8 : 1 ratio,

X_2 = true vapour pressure.

P_2 = apparent vapour pressure, so that mol. fraction

$$\text{hydrocarbon} = \frac{X_2}{P_2}$$

then
$$\frac{X_1}{P_1} = \frac{X_2}{P_2}$$

or
$$\frac{X_2}{X_1} = \frac{P_2}{P_1}$$

Reading the observed values of P_1 and P_2 from Graph 4,

$$\frac{X_2}{X_1} = \frac{\text{Apparent vapour pressure at 100° F. at 8 : 1 ratio}}{\text{Apparent vapour pressure at 60° F. at 2 : 1 ratio}}$$

$$= \frac{750}{338}$$

$$= 2{\cdot}22 = \frac{\text{true vapour pressure at 100° F.}}{\text{true vapour pressure at 60° F.}}$$

From equation 5 which has hitherto been assumed, or more conveniently from the derived curves shown in Graph 4, we find that if the vapour pressure at 60° F. is 146 mm., then at 100° F. it will be 311 mm. ; the ratio being $\frac{311}{146} = 2{\cdot}13$.

This is in fair agreement with the deduced ration of 2·22. Similarly,

At 80° F. and 2 : 1 ratio, A = 6020, P_1 = 412 mm.

At 125° F. and 8 : 1 ratio, A = 6020, P_2 = 930 mm.

$$\text{Ratio } \frac{X_2}{X_1} = 2{\cdot}26$$

while from the curves in Graph 4 based on equation 5, assuming 146 mm. at 60° F.

$$\frac{X_2}{X_1} = \frac{477}{215} = 2{\cdot}22$$

Thus the deviation from equation 5 is less than 5 per cent.

Recapitulating the results by calculation :—

	True Vapour Pressure.			
	Motor Spirit.		Aviation Spirit.	
	at 60° F.	at 130° F.	at 60° F.	at 130° F.
Method 1 ..	149mm.	525mm.	205mm.	695mm.
Method 2 ..	146mm.	531mm.	207mm.	717mm.

Methods 1 and 2 are thus in satisfactory agreement. Method 2 is based on sounder theoretical lines than method 1, since an independent check on the slope of the vapour pressure curve is obtainable. Method 1 is, however, more rapid.

The foregoing shows how a value for the true hydrocarbon vapour pressure may be arrived at without the necessity of effecting a physical separation of dissolved air.

It is, however, possible to estimate chemically the amount of air present in a vapour. This was done in the case of the motor spirit sample and aviation spirit sample investigated theoretically as shown. Owing, however, to the very small gas sample, the errors in gas analysis were unusually large; and the results, giving vapour pressures at 60° F. of 124 and 156 mm. respectively calculated on the oxygen content of the dissolved gases, are only of use in indicating the order of magnitude of the true vapour pressure.

The third factor associated with the vapour pressure phenomena of complex mixtures, *viz.*, the variation of vapour pressure with amount vaporised, may be briefly reviewed. The results obtained above indicate that this does not vary very greatly over the liquid/vapour ratios examined. This is in line with the conclusions of Brown,[2] and of Bridgeman, Aldrich and White.[7] At a fixed liquid/vapour ratio, however, the composition of the liquid will change slightly as the temperature is raised and more liquid is vaporised. Between 60° F. and 130° F. the vapour pressure increases approximately fourfold, so that the amount vaporised at 130° F. will be about four times that at 60° F. The same argument applies in comparing the amount vaporised at 60° F. at a 2 : 1 ratio with the amount vaporised at 60° F. at an 8 : 1 ratio. Since the variation in liquid composition in the latter case is small, it is probably equally small over the vapour pressure range investigated.

In determining vapour pressures by Andrews' apparatus at zero free space (5), no change in composition of the liquid occurs. By other methods, however, where a relatively large vapour space is used, *e.g.*, Rhodes and McConnell's method, or the Beistle-Prather bomb, the liquid composition is changed by the amount vaporised. Referring to the experimental results plotted on Graph No. 3, it is seen that the vapour pressure temperature curves by the latter methods do not deviate much from those by Andrews' apparatus. This indicates that over the temperature range and liquid/vapour ratios investigated in this paper, the effect of change of composition of the liquid in the case of gasolines and motor spirits is slight.

In regard to the calculation of true vapour pressure in the manner indicated, it may be noted that any experimental error in the observed vapour pressure determination may become an increased

error in the calculated result, as the following hypothetical case shows :—

Observed vapour pressure.			Calculated true vapour at 60° F. (Equations 5 and 10). (Method 1).
At 60° F.	At 130° F.		
500mm.	1000mm.	..	192mm.
510mm.	1000mm.	..	184mm.
Error + 2 per cent.		..	Error—4 per cent.

In some cases the true vapour pressure curve may deviate slightly from equation 5. In such a case the error by using method 1 may be minimised by calculating over two ranges of the observed vapour pressure curve to a common centre point. Method 2 affords a useful check.

It may be questioned, however, whether the errors inherent in eliminating by calculation the effect of dissolved air pressure, are not less than the errors introduced in effecting a physical separation of dissolved air by methods other than perfect fractionation.

It is concluded that over the temperature range and liquid/vapour ratios investigated, the observed vapour pressure curve of a gasoline or motor spirit containing dissolved air may be represented as follows :—

$$\text{Log } 10\ (P - aT) = 6{\cdot}76 - 3{\cdot}88\ \frac{t}{T}$$

where P = observed vapour pressure at an absolute temperature T.
t = constant = absolute temperature when the true vapour pressure is 760 mm.
a = Constant.

If P_1 P_2 are the observed vapour pressures at any two temperatures T_1 T_2 (the liquid/vapour ratio being constant), then the dissolved air pressure A at temperature T_1 is given by the equation :

$$T_2 \text{ Log } \left(P_2 - \frac{T_2}{T_1}A\right) - T_1 \text{ Log } (P_1 - A) = 6{\cdot}76\ (T_2 - T_1).$$

The equation may be solved graphically to evaluate A; after which the true vapour pressure at temperature T_1 may be found by difference.

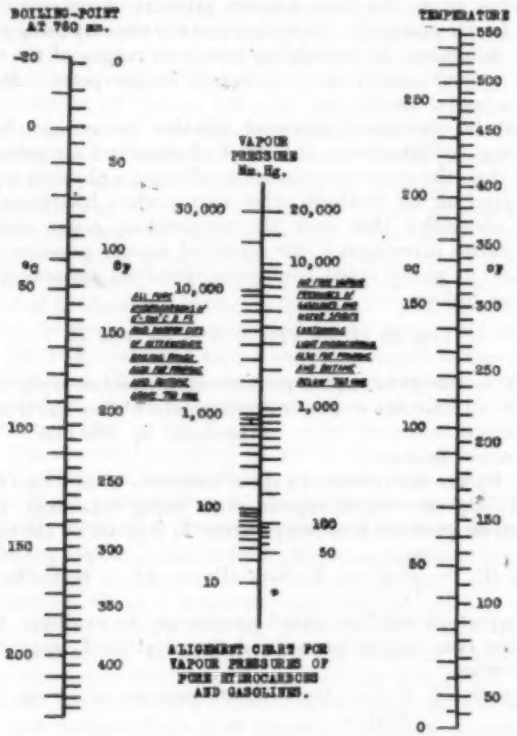
Alternatively, if x = true vapour pressure at temp. T_1,
$f(x)$ = " " " " " T_2,
then

$$f(x) + \frac{T_2}{T_1}(P_1 - x) = P_2,$$

which may be solved for x by correlating $f(x)$ with x over the expected range of x by the aid of equation 5 as has been done in this paper.

Relationships such as equations 2, 3, 4 and 5 are readily adapted to presentation as an alignment chart. For pure hydrocarbons from pentane and heavier, the chart gives results identical with the alignment chart of Wilson.[11]

The applicability of the methods of calculation shown is probably limited to the temperature range investigated. The method may be of use in matters regarding evaporation losses, transport and engine performance of light spirits.



Equation 5 applied to very high or very low pressures may, in some cases, give only an approximate value for the true vapour pressure, unless the extent of deviation from equation 5 has been determined by experiment.

Similar methods of analysis may be found possible in the case of crude oil, when sufficient experimental data has been collected

to justify the use of a standard vapour pressure curve on the lines of Graph 3.

The author's thanks are due to Messrs. the Anglo-Persian Oil Company, Limited, for permission to make use of a large amount of experimental data obtained at various centres of the Company's operations, and to Dr. F. B. Thole and Mr. E. S. L. Beale for their kind revision of this paper.

Note on Rhodes and McConnell's Results.

The correlation of a large amount of vapour pressure data not available at the time when Rhodes and McConnell originally worked out their method, makes possible a review of the results obtained. Experimental results given in Fig. 4 :—

V.P. at 10° C. ..	Original	187 mm.	Air Free	46 mm.
,, ,, 40° C. ..	,,	314 mm.	,, ,,	152 mm.
(Vide reference 6)				
V.P. at 10° C. ..	Original	137 mm.	Air Free	50 mm.
,, ,, 40° C. ..	,,	300 mm.	,, ,,	185 mm.
,, ,, 10° C. ..	,,	405 mm.	,, ,,	300 mm.
,, ,, 30° C. ..	,,	770 mm.	,, ,,	610 mm.

The true vapour pressure at 10° C. of the above spirits has been calculated by the first method given in this paper.

True Vapour Pressure at 10° C.

Calculated.	Observed.
56 mm.	46 mm.
79 mm.	50 mm.
(403) mm.	300 mm.

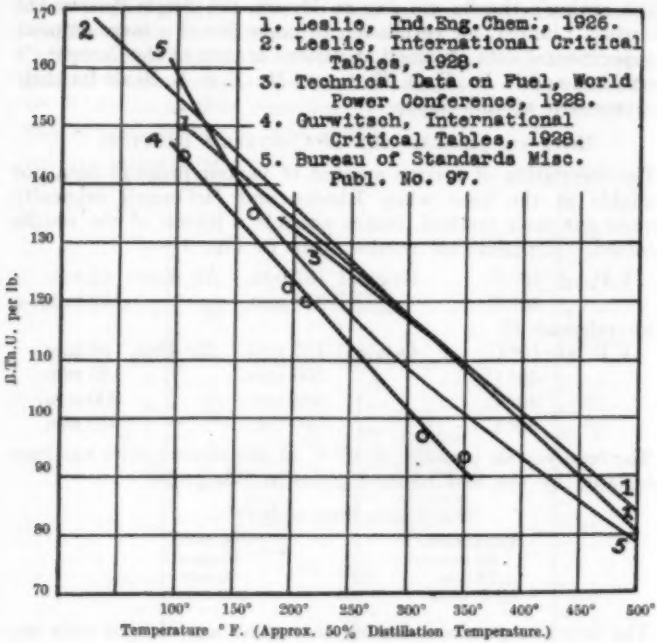
The first two results indicated that some loss of light ends was associated with the expulsion of dissolved gas. The last result is of interest; since the vapour pressure curve of the original spirit before expulsion of dissolved gas, is already a true hydrocarbon curve and fits Graph 3. The curve after expulsion of dissolved gas also fits Graph 3. This therefore indicates that only a negligible quantity of air was originally present in the sample. The spirit was a gasoline of high vapour pressure, and would not normally be expected to contain much dissolved air.

Note on the Latent Heat of Vaporisation and Molecular Weight of Petroleum Distillates.

Available data from various sources for the latent heat of vaporisation of petroleum fraction has been plotted on Graph No. 6.

The equation to curve No. 5 on this graph includes a density term; and in plotting this curve the boiling-point/sp. gr. relationship found by Fitz-Simons and Bahlke[12] has been employed.

In general the curves are in good agreement, with the possible exception of curve 4.



GRAPH 6.

DATA ON LATENT HEAT OF VAPORISATION OF PETROLEUM DISTILLATES

In regard to molecular weights, a satisfactory correlation between the 50 per cent. A.S.T.M. temperatures and the molecular weights of Mid-Continent crude fractions has been found by Fitz-Simons and Bahlke[12]:—

50 per cent. A.S.T.M. Temperature.		Molecular Weight.
0° F.	..	52
100° F.	..	75
200° F.	..	100
300° F.	..	128
400° F.	..	160
500° F.	..	205
600° F.	..	260
700° F.	..	325

TABLE SHOWING EXPERIMENTAL DATA OF AIR FREE VAPOUR PRESSURE OF GASOLINE AND MOTOR SPIRIT, PLOTTED ON GRAPH NO. 3.

Reference.	Experimental Method of Air Freeing.	Type of Vapour Pressure Apparatus.	T°	Vapour Pressure, Mm. Hg.	Boiling Point t interpolated.	Ratio $\frac{t\ (abs)}{T\ (abs)}$
(6)	Non-condensible gas removed by boiling under reduced pressure.	Rhodes and McConnell.	0° C.	380	23° C.	1·084
			10° C.	490		1·046
			51° C.	1500		0·914
			0°	280	28° C.	1·103
			10°	400		1·064
			50°	1420		0·932
			0°	215	35° C.	1·128
			10°	320		1·089
			20°	450		1·051
			50°	1180		0·954
			0°	190	38° C.	1·139
			20°	420		1·062
			10° C.	190	55° C.	1·164
(2)*	Calculated	Beistle	0° C.	580	10·8° C.	1·039
			50° C.	2150		0·379
	Air-Free.	Prather	0° C.	390	22·5° C.	1·082
			50° C.	1550		0·915
			60° C.	2020		0·887
			56° C.	1190	38·5° C.	0·947
			60° C.	1320		0·936
			80° C.	1840	45° C.	0·897
*	Refluxed.	Andrews' Apparatus.	15° C.	127	74° C.	1·205
			54° C.	438		1·061
			92° C.	1205		0·950
			133·5° C.	2873		0·854
			192° C.	7093		0·747
	None.	Andrews' Apparatus.	26° C.	1200	11° C.	0·950
			82° C.	4770		0·800
			122° C.	10180		0·719
(8)	Calculated air-free by graphical method.	Tizard and Marshall. Data by W. H. Cadman.	62° F.	388	101° F.	1·075
			78° F.	494		1·042
			75° F.	151	168° F.	1·173
			90° F.	190		1·142
			146° F.	518		1·036
			78° F.	137	180° F.	1·190
			90° F.	159		1·164
			128° F.	314		1·088
			154° F.	541		1·042
(7)	Application of Vacuum at low temperatures.	Andrews' Apparatus.	$\text{Log}_{10} P = 6{\cdot}76 - 3{\cdot}88 \frac{t}{T}$			

*Data courtesy, Messrs. Anglo-Persian Oil Company, Limited.

The results are all close to the boiling-point molecular weight curve for normal hydrocarbons, so that in all probability the results are of general applicability.

Using the various values for latent heat shown in Graph 6, and the above molecular weights, the value of Trouton's constant is found to be as follows :—

Temperature.	Mol. Wt.	Trouton's Constant.				
		Curve 1.	Curve 2.	Curve 3.	Curve 4.	Curve 5.
100° F.	75	20·2	20·8	—	19·6	21·4
150° F.	87	20·4	20·8	20·1	19·3	20·4
200° F.	100	20·4	20·7	20·2	18·9	19·6

The average value for curves 1, 2, 3, 5 is 20·4, which is the value of Trouton's constant for pure hydrocarbons.

The vapour pressure curves of mixtures of wide boiling range, such as motor spirit, are found to be in agreement with a value of Trouton's constant of 17·6. It is evident that this value is more apparent than real, and that the true latent heat of vaporisation corresponds to the normal value of 20—21.

References.

[1] Ormandy and Craven, *J. Inst. Petr. Techn.*, 1922, **8**, 162–163.

[2] Brown, Proc. 7th Annual Convention of the Natural Gasoline Association of America, 1928.

[3] Ashworth, *J. Inst. Petr. Techn.*, 1924, **10**, 787.

[4] Nernst has proposed the relationship Trouton's constant = 9·5 log t — 0·007 t.

[5] By " vapour pressure at zero free space " is meant the average between the pressure when a very small bubble of vapour is present, and the pressure just necessary to cause this small bubble of vapour to disappear.

[6] Rhodes and McConnell, *Ind. Eng. Chem.*, 1923, 1273, *et seq.*

[7] Bridgeman, Aldrich and White, Annual General Meeting of the *Soc. Auto. Engrs. Detroit*, Jan., 1929. Also Tenth Annual Meeting, A.P.I., 1929, Section III.

[8] The method was originally proposed by Tizard and Marshall, *J. Inst. Petr. Techn.*, 1922, **8**, 217 *et seq.* The data used in this paper is however that of Cadman for gasoline, aviation spirit, and petrol, *J. Inst. Petr. Techn.*, 1924, **10**, 947 *et seq.*

[9] Vide reference 7 above ; the authors give the equation as

$$\frac{t}{T} = 1 - 0{\cdot}2578 \log \frac{P}{760}$$

which has been transposed as shown for convenience.

[10] Vide International Critical Tables, 1928, III, 262–263.

[11] O. G. Wilson, Jr., *Ind. Eng. Chem.*, 1928, 1363.

[12] Tenth Annual Meeting, A.P.I., 1929, Section III.

KNOCK-RATING OF MOTOR FUELS.

Note on Experiments Carried out in 1930.

By The Sub-Committee of the Institution of Petroleum Technologists on Knock-Rating of Motor Fuels.

(To be read at the meeting of the Society of Automotive Engineers in Detroit during the papers on the position of Engine Testing of Motor Fuels.)

A short paper was read at the January, 1930, meeting of the S.A.E. dealing with tests carried out by the research laboratories of the Anglo-American Oil Company, the Anglo-Persian Oil Company and the Asiatic Petroleum Company with the object of determining the agreement which could be obtained on three widely different designs of test engine when the gasolines in common use on the British market were examined. It was realised that this range was comparatively narrow and that further work would probably be necessary. The results obtained encouraged the belief that reasonable agreement might be reached with a greater range of fuels. An extended programme was therefore planned and put into effect, and the results of the second series of tests were communicated to the C.F.R. Detonation Sub-Committee through Dr. Dickinson. These tests included the rating of five straight-run gasolines varying from a very low to a very high anti-knock value, a blend of high benzole content, blends containing vapour-phase and liquid-phase cracked spirit, a blend containing lead tetra-ethyl and an alcohol blend. The same three engines were used, viz., the Ricardo 2-litre E 35, the Delco and the Armstrong. In order to explore the effect of running technique as thoroughly as possible each fuel was tested:

A. with cold inlet air and normal jacket temperature;

B. with heated inlet air and normal jacket temperature;

C. with heated inlet air and the jacket cooled with ethylene glycol at about 375° F.

The fuel samples were rated in three ways:

(*a*) In terms of the blend of a high value and a low value straight-run gasoline required to match the sample.

(*b*) In terms of the equivalent benzene-heptane blends.

(*c*) In terms of the equivalent iso-octane-heptane blends.

The agreement reached during the first series of tests was repeated fairly closely for the second series of straight-run gasolines, when results were expressed in terms of the high and low value straight-run gasoline sub-standards, but the results differed more when the fuels were rated in terms of the pure hydrocarbons and there was pronounced disagreement in the cases of the fuels which were not straight run.

No particular variation appeared to be caused by the use of the throttling method as compared with the variable compression method, but the agreement was definitely improved when the inlet air was heated to about 120° F. before entering the carburettor. This appears to be preferable to the application of unlimited heat in the manifold.

It was agreed that the bouncing pin was the most satisfactory means for measuring knock intensity if the engine was small enough for it to function properly.

The results obtained tended to show that iso-octane, at least in the two engines which used this standard, gave a greater degree of fluctuation in knock intensity, as against benzene, but this is obviously a point which can only be decided in reference to the particular engine and technique ultimately adopted. We understand that tests on the Horning engine have shown iso-octane to be rather more consistent than benzene and, therefore, members of the Sub-Committee of the Institution of Petroleum Technologists have agreed that, in future, all knock ratings of gasolines shall be expressed in terms of the octane number.

Reverting to the test results from the three British engines, it was at once obvious that there was little hope of correlating the majority of existing types of testing plant with the new standard engine, although correlation should be possible if determined separately for each type of fuel used. Some such correlation will probably be necessary to bridge over the period during which laboratories in all parts of the world are making changes from their existing plant to the new standard.

The laboratories concerned in these tests have experimented both with coil and magneto ignition, and their opinion is unanimously in favour of the former, which has given steadier firing and is generally more dependable if a suitable coil is used. The chief technical objection to the magneto is the variation in flux density, on account of both ageing and timing adjustment. It is felt that the problem of battery charging is of minor importance compared with consistent behaviour and it is presumed that in this matter, as in all others where the final decision has yet to be made, the necessity for accuracy will be put before any considerations of simplicity of either technique or construction. In such an instrument as a

fuel-testing engine simplicity and accuracy do not invariably go together.

It seems desirable, whatever the decision reached regarding the use of the variable compression or the throttling method, that the engines should be available with both arrangements when required, since many laboratories will be desirous of carrying out special investigations apart from any standard method which may be laid down.

The Anglo-American Oil Company already has a Horning engine in its laboratory, and this is to be brought into line with the latest developments as soon as possible. It is hoped that the other two laboratories will have similar engines in a short time, and as soon as these are installed a further programme of work will be arranged in collaboration with the C.F.R. Detonation Sub-Committee. Active steps are being taken to enlist the co-operation of other interested organisations in Great Britain and in Europe, and it is hoped that in the not far-distant future a considerable practical advance will have been made towards the international use of the standard engine.

BOOKS RECEIVED

REPORT OF THE FUEL RESEARCH BOARD FOR THE YEAR ENDED MARCH 31ST, 1930. Pp. 121 + viii. H.M. Stationery Office, 1930. 2s. net.

This report also includes that of the Director of Fuel Research, and this deals in full with the activities of the Fuel Research Board during the period under review. The subject headings are the National Coal Resources, Coal Examination and Laboratory Investigations, High Temperature Carbonisation and Gasification, Low Temperature Carbonisation, Coke, Pitch and Briquetting, Purification of Coal, Hydrogenation, Domestic Heating, Internal Combustion Engines, Miscellaneous Laboratory Work and Miscellaneous, and serve as a brief indication that the book is one which can be read with interest and advantage by all fuel technologists.

BRITISH CHEMICALS AND THEIR MANUFACTURERS. Association of British Chemical Manufacturers. Pp. 405. London, 1931.

The Association of British Chemical Manufacturers have just published a new edition of their volume on "British Chemicals," copies of which are obtainable gratis by genuine users of chemicals on application to the Association at 166, Piccadilly, London, W. 1.

The main purpose of this book is to act as a Directory of the products of the Members of the Association and its value to users of chemicals is increased by its being printed in six languages, viz.: English, French, German, Italian, Portuguese and Spanish. Not only are the 234 pages of the Classified List printed in these languages, but five separate indices are given in the five foreign languages. A Table of Proprietary and Trade Names, occupying 50 pages, is also provided, and the value of this is obvious.

The Association is to be congratulated on having performed a valuable service, not only to their Members, but to users of chemicals and chemical products all over the world.

OFFICIAL DIRECTORY OF THE BRITISH CHEMICAL PLANT MANUFACTURERS' ASSOCIATION, 1931. Pp. 151. London, 1931.

To users of chemical plant this volume should prove of great value in providing a ready guide to the products of British chemical plant manufacturers. Over 50 pages are devoted to a Classified List of Products and Services offered by Members of the Association, and a perusal of the book will show that British manufacturers are able to supply the best types of plants, incorporating the latest scientific principles in their design.

Genuine users of chemical plant may obtain a copy of the Directory free of charge on application to the Association at 166, Piccadilly, London, W. 1.